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REFINING OF MILITARY JET FUELS FROM SHALE OIL PART III
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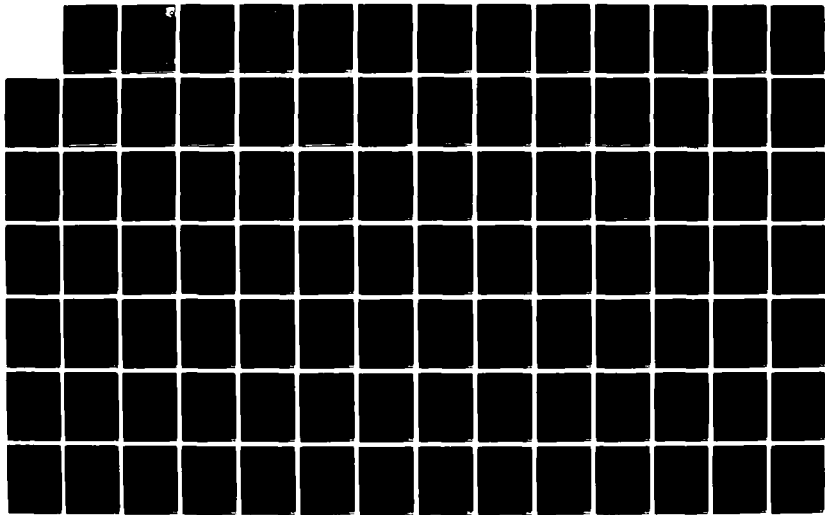
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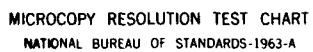
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AFWAL-TR-81-2056
Part III



REFINING OF MILITARY JET FUELS FROM SHALE OIL

Part III
Pilot Plant Sample Preparation

F. H. Turrill

ASHLAND PETROLEUM COMPANY
ASHLAND RESEARCH AND DEVELOPMENT
ASHLAND, KENTUCKY 41101

JULY 1982

INTERIM REPORT FOR PERIOD NOVEMBER 1979 - JUNE 1981

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Phase III work performed was aimed at confirming final process design estimates proposed in Phase I and producing sample lots of turbine fuel for aircraft performance evaluations. Drum quantities of JP-4, JP-8 and Broadrange jet fuel were supplied to AFWAL, along with a gasoline blending component, diesel fuels, and residual fuels for these evaluations. Also, the scaled-up data from Phase III operating data were utilized in the Phase IV Economic Evaluations.		

FOREWORD

This project was sponsored by the U.S. Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, under Contract No. F-33615-78-C-2080. The work herein was performed during the period of November 15, 1979 to June 30, 1981 under Program Elements 62203F and 63215F, Work Units 30480504 and 24800004, respectively.

Part III describes the effort of Ashland Petroleum Company Research and Development personnel in the pilot scale preparation of fuel samples derived from crude shale oil.

While the many persons who contributed to the successful completion of this contract phase are too numerous to list by name, the author wishes to specifically acknowledge the contributions of the following individuals: Dr. William P. Hettinger, Jr., Vice-President and Director of Research; Mr. Estel M. Hobbs, Director of Ashland's Automotive Products Application Laboratory; Mr. William A. Sutton, principal investigator for the contract; Mr. Don M. Lee, Manager of the R&D Pilot Plant; Mr. S.D. Kenyon, Research Engineer with the Ashland Pilot Plant; Mr. Howard F. Moore, Manager of the R&D Synthetic Fuels Group; and Mary E. McIntyre, Research Engineer, formerly of Ashland's Pilot Plant.

Special recognition is due to Mr. Wayne D. Pinkston, who served as the first Phase III project leader and who is presently employed by Cities Service. Mr. Pinkston was responsible for much of the work cited in this report. The helpful suggestions of our Air Force contract monitors, Dr. Ron Butler and Mrs. Charlotte Eigel, were greatly appreciated and were of material benefit in the successful conclusion of this phase. Last, but by no means least, we gratefully acknowledge the many hours of dedicated work by Mrs. Carolyn Honaker and Mrs. Teri Haberek in typing this report.

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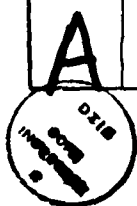


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ABBREVIATIONS

A	Aromatics
AFAPL	Air Force Aero Propulsion Laboratory
AFWAL	Air Force Wright Aeronautical Laboratories
API	American Petroleum Institute
ASTM	American Society for Testing Materials
bbl	Barrel
BPSD	Barrels per Stream Day
BR NO.	Bromine Number
B/D	Barrels Per Day
C ₁	Methane
C ₂	Ethane
C ₃	Propane
C ₃ ⁼	Propylene
n-C ₄	Normal Butane
i-C ₄	Isobutane
C ₄ ⁼	Butylene
C ₅	Pentane
C ₅ 's	Pentane and Pentenes
C ₅ ⁺ , >C ₅	Compounds Heavier than Pentane in Gas Streams
C ₆	Hexane
C/H	Carbon-to-Hydrogen Ratio
CO	Carbon Monoxide or Cycle Oil
C/O	Catalyst-to-Oil Ratio

ABBREVIATIONS (CONT'D)

COHT	Cycle Oil Hydrotreater
Co/Mo or CoMo	Cobalt Molybdate Catalyst
CR	Cracked
CSHT	Crude Shale Oil Hydrotreater
cSt	Centistoke
CW	Cooling Water
EP	End Point in a Distillation
EXTD	Extracted
FI	Flow Indicator
FIA	Fluorescent Indicator Adsorption - Test Method to Determine Hydrocarbon Types, ASTM D1319
FIC	Flow Indicator Controller
FT	Flow Transmitter
GCHT	Guardcase Hydrotreater
HC	Hydrocarbon
HC/N	Hydrocarbons-to-Nitrogen ratio
Hydrog.	Hydrogenated
IBP	Initial Boiling Point
I.D.	Inside Diameter

ABBREVIATIONS (CONT'D)

JP-4	Military Specification MIL-T-5624K Turbine Fuel
JP-8	Military Specification MIL-T-8333 Turbine Fuel
JP-8 Broadrange	Experimental Turbine Fuel Having a Higher Aromatics Content than JP-8
LHSV	Liquid Hourly Space Velocity
LV%	Liquid Volume Percent
MAX	Maximum
MIN	Minimum
min	Minute
MRCC	Modified Reduced Crude Conversion
Ni/Mo or NiMo	Nickel Molybdate Catalyst
NO.	Number
n-PARAFFIN	Normal Paraffin
O	Olefins
ON SPEC	Meeting Specifications
P	Pressure
PI	Pressure Indicator
PIC	Pressure Indicator/Controller
PT	Pressure Transmitter



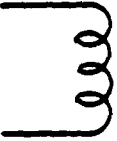




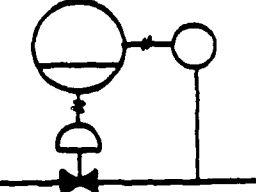
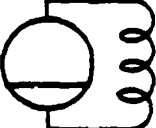


ABBREVIATIONS (CONT'D)

Pt/Al	Platinum (on Alumina) Catalyst
Pt/Re	Platinum/Rhenium (on Alumina) Catalyst
R&D	Research & Development
REGEN	Regenerator Section of FCC
RVP	Reid Vapor Pressure
S	Saturates
SCFB	Standard Cubic Feet per Barrel
SCFH	Standard Cubic Feet per Hour
SIM-D	Simulated Distillation
SS	Stainless Steel
SU or SUS	Saybolt Universal Seconds
TIC	Temperature Indicator and Controller
TEL	Lead Antiknock Compound
VIS	Viscosity
VOL	Volume
VOL %	Volume Percent

SYMBOLS

=	Equals
+	Positive, plus, or greater than as in 600°F+
-	Negative, minus, or less than as in -600°F
%	Percent
>	Greater Than
<	Less Than
"	Inches
#	Number or Pound
Δ	Difference

LEGEND FOR UNDEFINED SYMBOLS
USED IN UNIT DRAWINGS

	Valve
	Control valve
	Electric heater or steam coil
	Board mounted controller, type as indicated
	Local indicator (type as indicated)
	Transmitter (type as indicated)
	Transmission line
	Board mounted control system (type as indicated)
	Board mounted temperature control system
 Coolant	Heat exchanger
	Pump

SUMMARY

A complete pilot scale EXTRACTACRACKING sequence has been performed using Occidental in situ shale oil. Samples of specification JP-4, JP-8, and Broadrange JP-8 turbine fuels were produced and delivered to the Air Force, together with samples of diesel fuel, gasoline, and residual fuel blending components. Data relating to the production of these samples is contained in this report.

SECTION I
INTRODUCTION

On February 15, 1979, Ashland Petroleum Company, Research and Development Department, began work under contract F33615-78-C-2080, An Exploratory Research and Development Program Leading to Specifications for Aviation Turbine Fuel from Whole Crude Shale Oil. This program, funded by the Department of Defense, is designed to evaluate the EXTRACTACRACKING process as a potential improvement in shale oil refining technology.

EXTRACTACRACKING is a novel, integrated process developed by Ashland Petroleum Research consisting of a proprietary combination of hydrotreating, modified reduced crude conversion, acid extraction, freeze point modification, and product upgrading sequences. A simplified block diagram of this process is shown in Figure 1. More complete descriptions of this process may be found in the Phase II Interim Technical Report (AFWAL-TR-81-2056, Part II, Volumes I, II, and III).

This report describes the work carried out under Phase III of the above contract in the Ashland Research and Development Department Pilot Plant.

The objectives of this Phase III effort were:

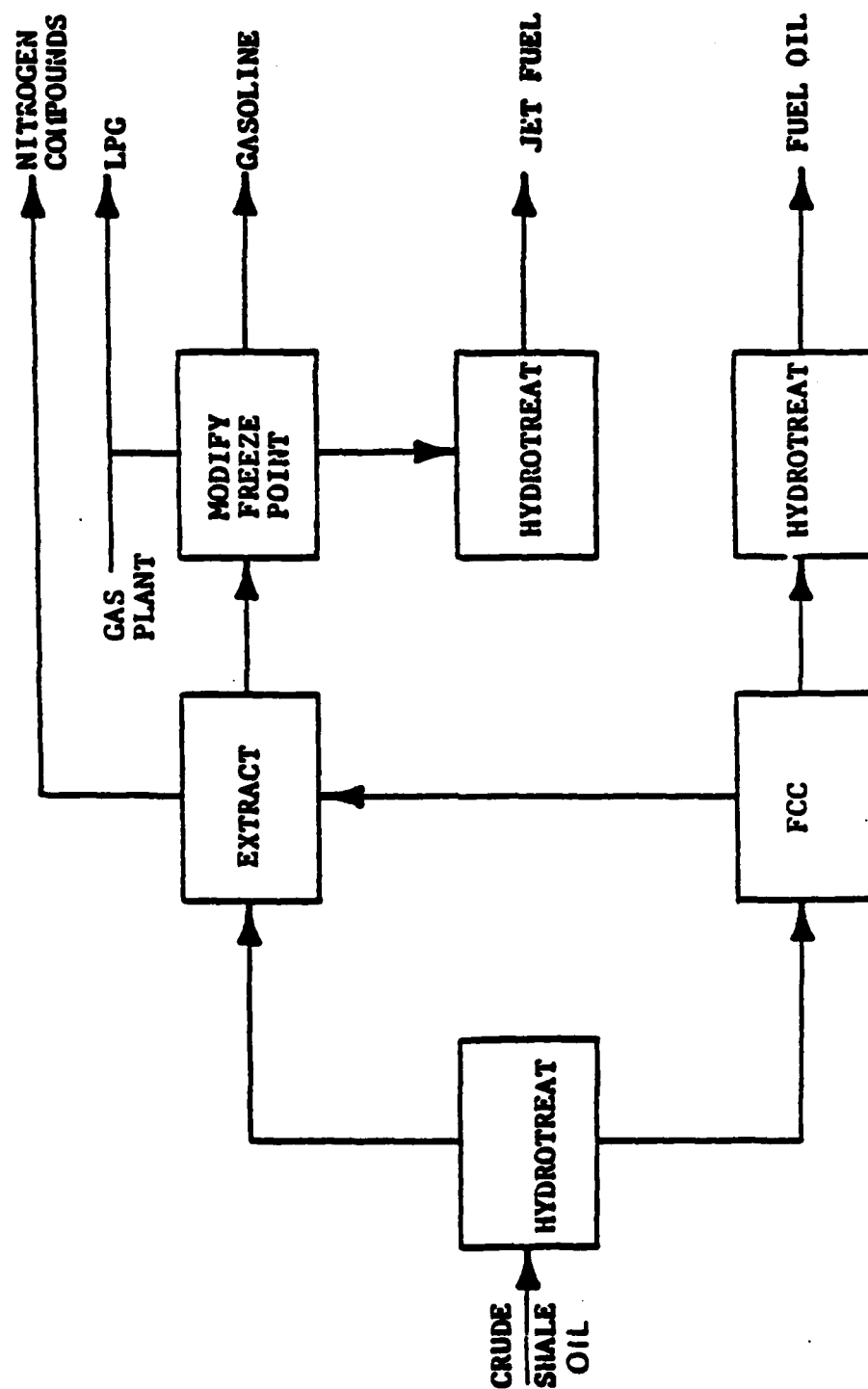


Figure 1. The EXTRACT cracking Process

- A. Develop scale-up and catalyst life data for use in the Phase IV Economic Analysis portion of the contract.
- B. Provide larger quantities of turbine fuels, and related diesel, gasoline, and residual fuel blending components for Air Force evaluation.

The initially established sample volume requirements included the production of approximately 300 gallon quantities of JP-4, JP-8, and Broadrange JP-8 turbine fuels. These requirements were reduced to 100 gallon quantities by the Air Force in February 1981 on the basis of budgetary restrictions.

The processing conditions used during Phase III were determined on the basis of Phase II results, modified as necessary on the basis of scale factors and product quality requirements.

SECTION II

CRUDE SHALE OIL FEEDSTOCK

1. SOURCE OF CRUDE SHALE OIL

The shale oil employed in the Phase III processing sequence was Occidental Petroleum's in situ oil produced during the Retort 6 run. A total of 61 drums of this material, having a net weight of 22,093 pounds, were withdrawn from storage for processing in Phase III.

2. SCOPE OF CRUDE SHALE OIL ANALYSIS

The crude shale oil analyses carried out in support of Phase III operations were less extensive than those employed during Phase II. The crude shale oil was spot checked to determine uniformity, and to establish correspondence with Phase II analytical results. For a more detailed analysis of Occidental's in situ oil, the reader is referred to the Phase II results contained in AFWAL-TR-81-2056, Part II, Volume II.

3. EXPERIMENTAL

Analyses were carried out concurrently with processing of the crude shale oil. During the early processing work, each drum of crude shale oil was analyzed. Later, because of the heavy analytical work load, and because of the relative consistency from drum to drum, this practice was limited to characterizing each fourth to fifth drum.

The drums were warmed to approximately 100°F using a band-type drum heater, the drum agitated, and a sample withdrawn through a spigot on the drum cap. Samples were submitted for analysis without filtration or dewatering.

4. EXPERIMENTAL RESULTS

The crude shale oil analytical results are shown in Tables 1 and 2.

5. DISCUSSION

The majority of the analytical determinations were performed within the Research Department, although some analyses were performed by independent analysts because of internal equipment limitations.

Significant disagreement was observed between the total nitrogen results obtained by Micro Kjeldahl analysis, and those obtained using ANTEK (Pyro-chemiluminescence) procedures. The reasons for this disagreement are uncertain, but may include differences in the relative interference by elements, such as sulfur, in the two techniques. Total nitrogen values, reported for the crude shale oil drums used in CSHT periods 1-23, were performed using a mixture of the two techniques. The total nitrogen values, reported for the crude shale oil drums CSHT periods 24-53, were determined using the ANTEK procedure, calibrated to agree with Micro Kjeldahl results. These remarks also apply to the CSHT product analyses performed during the respective periods.

TABLE 1
CRUDE SHALE INSPECTIONS

ITEM	DRUM IDENTIFICATION, RDA NO-										
	5578	5579	5580	5581	5582	5583	5618	5621	5664		
API	23.6	23.8	23.6	23.6	23.7	23.8	23.6	24.0	23.5		
Nitrogen, Wt %	1.47	1.58	1.64	1.50	1.36	1.53	1.37	1.61	1.43		
Basic Nitrogen, Wt %	0.96	0.84	0.92	0.86	0.94	0.99	0.81	0.89	0.89		
Sulfur, Wt %	0.72	0.72	0.65	0.68	0.72	0.74	0.78	0.48	0.68		
Oxygen, Wt %	-	-	-	-	0.88	-	-	-	0.89		
Hydrogen, Wt %	-	-	-	-	11.9	-	-	11.9	11.8		
Iron, ppm	-	68	68	-	69	-	-	73	67		
Nickel, ppm	-	-	-	-	1	-	-	11	11		
Vanadium, ppm	-	-	-	-	<1	-	-	1	<1		
Arsenic, ppm	-	31	31	-	46	-	-	44	27		
Chloride, ppm	-	-	-	-	25	-	-	-	22		
Ramsbottom Carbon	-	-	-	-	1.16	-	-	-	1.10		
Gross Heating Value, Btu/lb	-	-	-	-	18,709	-	-	18,732	18,725		
Applicable To Run Periods	Lineout	1-3	1	1-3	4-13	4-13	4-13	4-13	14-23		

TABLE 1 (CONT'D)
CRUDE SHALE INSPECTIONS

ITEM	DRUM IDENTIFICATION, RDA NO-										
	5701	5732	5753	5803	5808	5841	5869	5889	5926		
API	23.8	23.8	23.8	23.9	23.8	23.9	23.7	24.0	23.7		
Nitrogen, Wt %	1.35	1.37	1.31	1.31	1.21	1.70	1.31	1.63	1.36		
Basic Nitrogen, Wt %	0.85	0.85	0.82	0.83	0.81	0.88	0.85	0.86	0.78		
Sulfur, Wt %	0.67	0.67	0.55	0.52	0.52	0.72	0.74	-	0.71		
Oxygen, Wt %	0.92	0.88	0.93	0.98	1.01	0.96	1.01	1.05	0.98		
Hydrogen, Wt %	11.9	12.0	12.0	12.1	11.9	12.0	12.0	12.0	12.0		
Iron, ppm	72	65	62	73	75	72	70	74	29		
Nickel, ppm	12	10	10	10	13	13	12	13	3		
Vanadium, ppm	1	2	1	2	1	1	1	1	<1		
Arsenic, ppm	23	30	28	21	20	24	24	22	26		
Chloride, ppm	48	84	63	59	51	38	7	15	13		
Ramsbottom Carbon	1.00	1.05	1.05	1.01	1.05	1.02	-	1.05	1.01		
Gross Heating Value, Btu/lb	18716	18692	18670	18603	18586	18689	18762	18763	18693		
Applicable To Run Periods	14-23	14-23	24-36	24-36	24-36	37-54	37-54	37-54	37-54		

TABLE 2
CRUDE SHALE INSPECTIONS

	DRUM IDENTIFICATION, RDA NO-											
	5582	5621	5701	5732	5753	5803	5808	5869	5889	5841	5926	
Distillation, D 2887, °F												
IBP	323	304	319	380	326	301	317	350	359	324	334	
1 Wt %	346	344	344	400	349	337	341	375	373	346	353	
5	422	428	419	458	422	415	418	437	431	422	422	
10	465	468	460	498	464	453	457	476	470	464	464	
20	525	520	520	556	522	513	518	530	526	523	522	
30	578	572	574	597	576	560	573	578	575	578	576	
40	626	607	621	640	623	605	618	625	620	624	623	
50	674	652	667	633	669	651	666	670	668	672	670	
60	725	699	716	729	716	698	714	719	716	721	720	
70	777	751	768	777	767	747	767	769	768	774	772	
80	827	806	819	825	817	796	820	819	819	825	824	
90	884	867	873	879	869	847	876	871	877	880	881	
95	929	914	913	920	906	874	918	910	922	923	927	
99 Wt %	965	951	945	946	941	905	953	943	958	958	965	
EP	974	958	950	951	943	910	959	946	966	965	976	

The drum-to-drum variations shown in Tables 1 and 2 reflect experimental errors in both sampling and analysis, as well as actual compositional differences. It should be noted, however, that the average component levels fall close to those determined in Phase II.

SECTION III
CRUDE SHALE HYDROTREATING

1. OBJECTIVE

The objective of crude shale hydrotreating in the EXTRACTACRACKING process is to prepare the feedstock for subsequent acid extraction and modified reduced crude conversion operations through:

- A. Desulfurization
- B. Demetallization
- C. Olefin Saturation
- D. Denitrogenation
- E. Deoxygenation
- F. Conversion of non-basic nitrogen containing compounds to those containing basic nitrogen so as to enhance their removal during acid extraction and cracking operations.

The low severity conditions employed are intended to carry out functions A-F with as little hydrogen consumption as possible.

Crude shale oil hydrotreating in Phase III was performed, at reaction conditions considered optimum based on results from Phase II work, in order to provide feedstock for further processing and to obtain catalyst aging data. Parameter variation hydrotreating was not a Phase III

objective and the reader is referred to Phase II results published in AFWAL-TR-81-2056, Part II, Volumes I, II, and III for this data.

2. MECHANICAL DESCRIPTION

Crude shale oil hydrotreating was performed using the reactor configuration shown in Figure 2. Preheated feed and hydrogen were mixed and passed in an upflow manner through a guardbed consisting of activated high surface area alumina chips, and then to a trickle bed downflow reactor having a nominal diameter of 1.8" and a catalyst bed length of 97". In the reactor the oil-hydrogen mixture passed successively through a preheat zone of tabular alumina, a reaction zone containing the hydrotreating catalyst, packed in a manner proprietary to Ashland Oil, and finally through a post reaction zone of tabular alumina before being discharged into the low pressure stripping section of the unit through a back pressure control valve. The operation of the back pressure control valve was protected by the addition of water to the reactor discharge to prevent the build-up of salts, and by a filter system which retained catalyst fines and other particulate matter. The low pressure reaction product liquid was stripped of ammonia and hydrogen sulfide in a stripper section consisting of a 4" diameter column packed with Berl saddles, and employing a low pressure steam coil in the reboiler to maintain the desired temperature. The liquid bottoms product of the stripper was collected for fractionation. The gas stream from the stripper was cooled

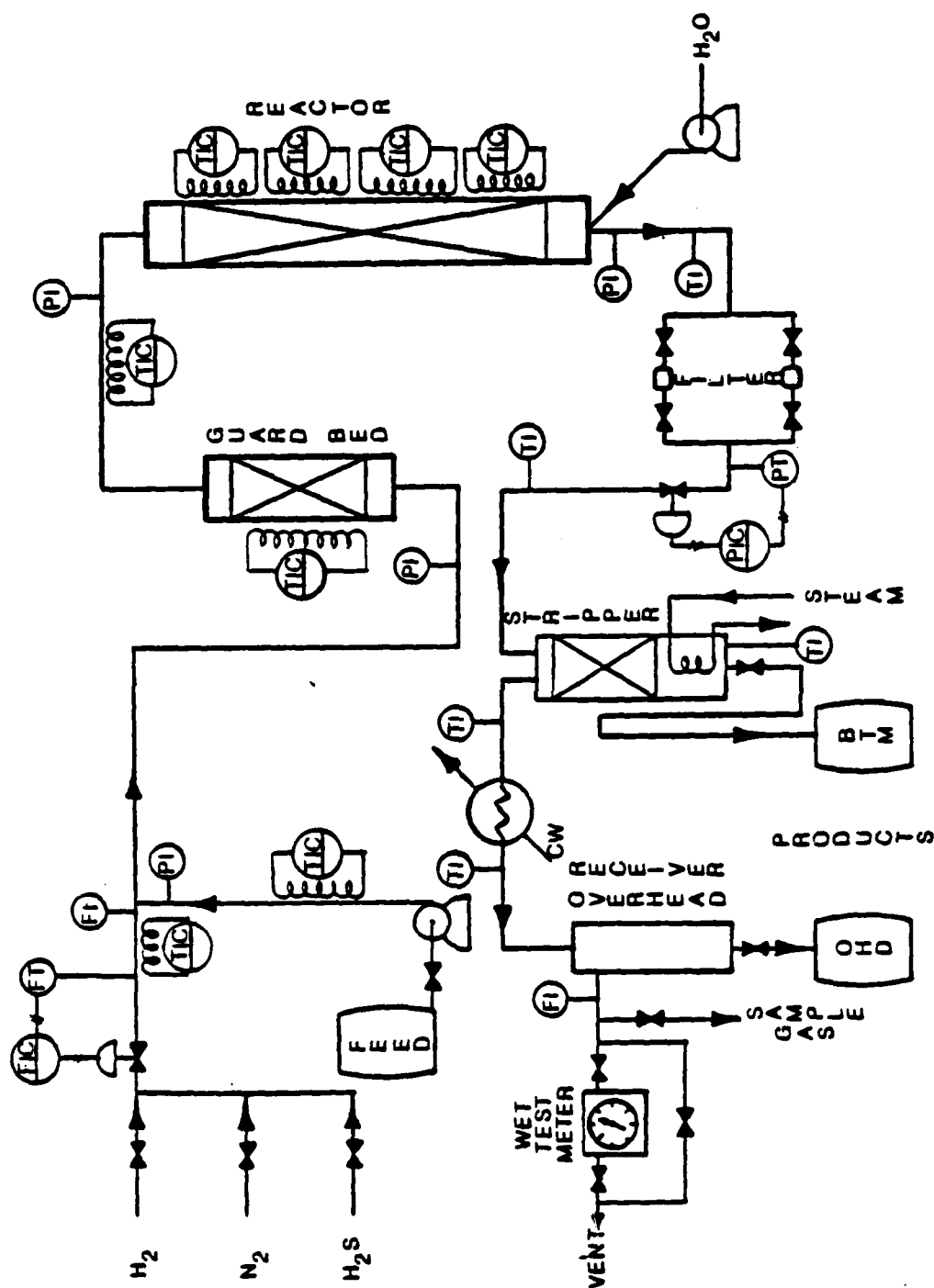


Figure 2. Crude Shale Hydrotreater

in a heliflow exchanger and the final gas-condensed liquid disengagement was accomplished in the overhead receiver. The condensed liquid was withdrawn and stored for blending with extraction feedstock without additional fractionation. A compressor, not shown, provided a hydrogen gas mixture at the desired reactor pressure. A thermowell containing five equally spaced thermocouples was placed in the center line of the reactor to permit monitoring of catalyst bed temperatures. A thermowell containing four thermocouples permitted similar measurement of guardbed temperatures. Other control features are shown on Figure 2.

3. CHEMICAL/CATALYST DESCRIPTION

The catalyst employed was a commercial cobalt/molybdate hydrotreating catalyst in the form of 1/16" extrudates. Except for minor variations in procedure, which will be given for specific catalyst loadings in the experimental section, the reactor was charged with an inert tabular alumina so as to provide a 3" layer for post heat and for support of the catalyst bed. The hydrotreating catalyst (approximately 1.0 gallon) was charged in one portion to provide a bed length of approximately 97". The remaining 3" at the top of the reactor bed was filled with tabular alumina to serve as a preheat section.

The guardbed consisted of 0.5 gallon of 8-14 mesh, high surface area, activated alumina chips. The bed was sandwiched between layers of tab alumina or alumina balls. The

charge was blown free of fines using dry nitrogen, and used without further activation.

4. FEEDSTOCK

The feedstock employed in this operation was Occidental in situ shale oil, the analysis of which was discussed in Section II. The representative analyses of the drums charged to the crude shale hydrotreating periods are detailed in Tables 1 and 2. The feedstock charge was maintained at approximately 100°F using a drum heater.

5. EXPERIMENTAL

The crude shale was hydrotreated at nominal conditions of 680°F, 1250 psig, 1.4 LHSV, and a gas circulation rate of 3800 SCFB. The guardbed temperature was maintained at a nominal temperature of 520°F.

Three charges of hydrotreating catalyst were used during the total processing sequence. The operating periods included for these charges and pertinent charging details are as follows:

Periods 1-3

In this charging, an attempt was made to void-fill the catalyst charge using a technique proprietary to Ashland Oil. The hydrotreating catalyst (0.359 gallon)

and void-filling material had a combined bed length of 97". Three-inch sections of tabular alumina were used as preheat and post reaction sections. This configuration plugged very rapidly and was not further employed.

Periods 4-23

No void fill was employed. The hydrotreating catalyst (1.049 gallon) was sandwiched between 3" preheat and postheat sections of tabular alumina.

Periods 24-53

Charging was similar to that used in periods 4-23 except the hydrotreating catalyst volume was 1.017 gallon.

Pressure checking and sulfiding procedures were common to all catalyst charges. The assembled reactor system was pressure tested to 1400 psig with nitrogen, then hydrogen. Following correction of any leaks found, the catalyst was presulfided in flowing H_2S at 120 psig and 725°F, and blocked in at this temperature for two hours. The reactor was cooled in flowing hydrogen at atmospheric pressure until close to room temperature. The hydrogen rate and reaction pressure were set and the unit heated to approximately 300°F. Feed was initiated and the system was brought slowly to the desired operating conditions.

The guardbed, which was intended to remove arsenic, iron, and other metals from the shale oil feed before entering the reactor preheat zone, was recharged following Period 23 and Period 36. The reactor had a nominal diameter of 1.8" and was charged as follows:

Periods 1-23

A 3" layer of tabular alumina was charged to serve as a support for the activated alumina and to serve as a preheat section. The 8-14 mesh activated alumina chips (0.514 gallon) were charged to yield a bed length of 37", followed by a 3" tabular alumina postheat section. A free space of 6" was left at the top of the bed.

Periods 23-36

The preheat section at the bottom of the reactor consisted of a 5" layer of 1/4" alumina balls, the activated alumina had a volume of 0.501 gallon, and the postheat section comprised a 2" layer of 1/4" alumina balls. As before, a 6" free space was left at the top of the bed.

Periods 36-53

Same as previous load except that the activated alumina volume was 0.508 gallon.

In all cases above, the activated alumina bed was blown free of fines using dry nitrogen and used without further activation.

Conditions were measured continuously and adjusted as required to maintain the desired operating levels. Hourly recording of all pertinent weights, temperatures, pressures, and flows were maintained.

The specific operating period was defined as the time required to produce a drum of reactor product, and averaged 38-40 hours in length. The product from each period was subjected to analysis for sulfur, nitrogen, and °API. Composites consisting of from four to six operating periods were subjected to more detailed analyses. The bottoms stream from the stripper was split at 600°F using the fractionating column shown in Figure 3 in reduced pressure mode. The column was 4" in diameter and contained a 20' section of 1/2" pall rings. The overhead stream from the reactor stripper was not subjected to further fractionation and was blended with the <600°F fractionator overhead for use as a feedstock for acid extraction. The >600°F bottoms from this fractionation were used as feedstocks for modified reduced crude conversion.

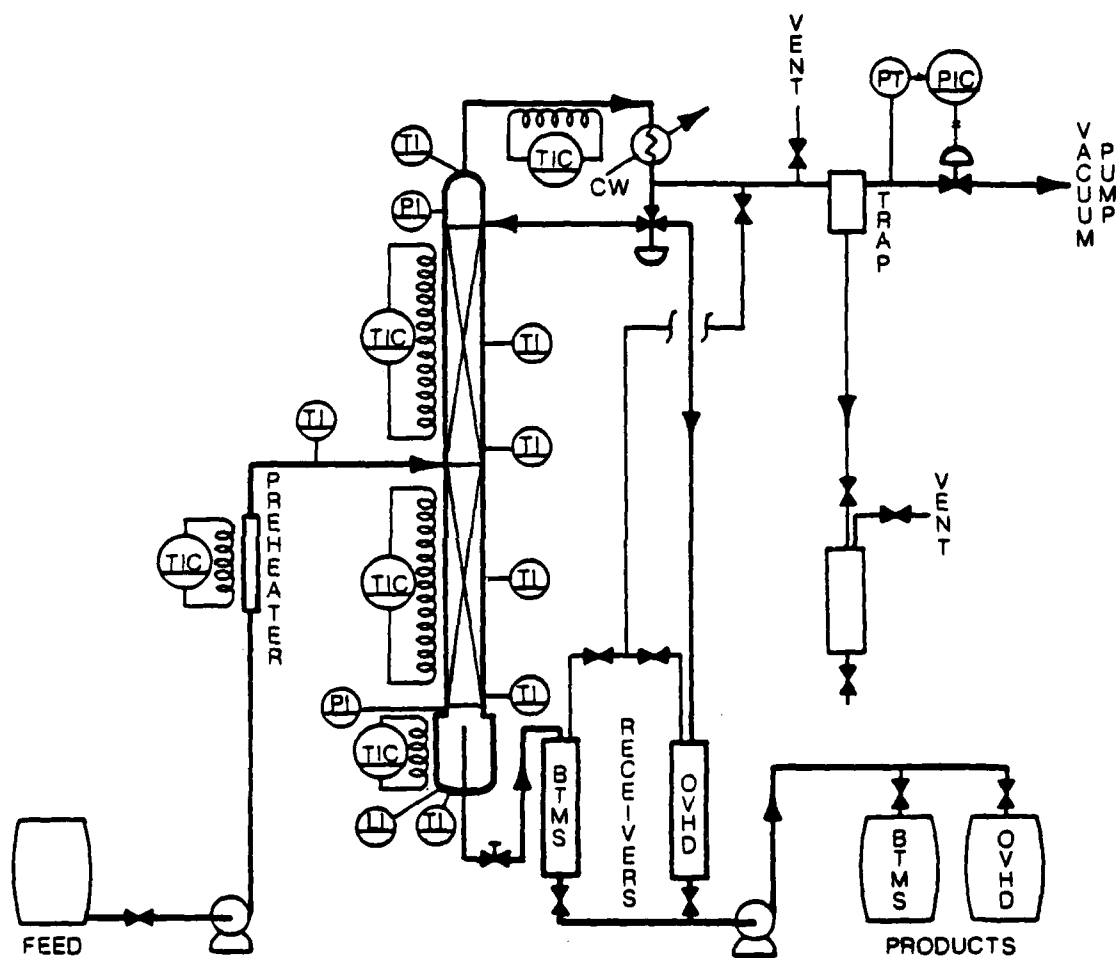


Figure 3. Fractionation Column

6. RESULTS

A chronological description of the crude shale hydro-treating operations is shown in Table 3.

The major problems which were encountered were reactor plugging, low refinery hydrogen supply pressure and hydrogen content, and feed pump problems. Minor leaks were corrected as they occurred.

The operating conditions used and the results obtained for the operating periods are listed in Table 4 and shown graphically in Figures 4 and 5. The temperatures shown for the reactor and for the guardcase are averaged over the entire bed. The liquid properties shown are those for the entire liquid reaction product, including both stripper overhead and stripper bottoms, and the recovery value listed is for this total stream as a weight percent of the crude shale charge. Because of the short run length, and because of the severe operating problems encountered in operating periods 1-3, the results of this portion of the crude shale hydrotreating operation were considered atypical, and were omitted from the data base. The products produced were, however, used in further processing.

The same difficulties which were encountered in nitrogen analysis of crude shale oil were also encountered in the analysis of the crude shale oil hydrotreater product, and the comments in Section II are applicable.

(Continued on page 35)

TABLE 3
CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
5/7/80	-	Loading, pressure checking, and calibration.
5/8/80		Presulfiding of catalyst.
5/9/80	1130	Start lineout/adjustment period.
5/9/80	1530	Shut down due to line plugging.
5/12/80	1630	Restart after maintenance.
5/13/80	0700	End lineout, start test period 1. Stream time at start of period 1, 38.5 hours because of intermittent feed problems.
5/15/80	0300	End test period 1.
	0300	Start test period 2.
5/16/80	1030	End test period 2. Unit shut down because of plugging and leaks.
5/21/80	0900	Restart unit after maintenance.
5/21/80	1700	Start test period 3.
5/22/80	0030	Unit shutdown because of reactor and control valve problems. Cata- lyst bed in reactor badly plugged on inspection.
5/27/80	-	Charge reactor with fresh catalyst. Carry out pressure checking and calibration.
5/28/80		Presulfide catalyst.
5/29/80	1200	Start lineout/adjustment period.
5/30/80	1000	Start test period 4.
	1000	Problems with hydrogen supply pressure required operation at lower pressure than desired, 1250 psig.
5/30/80	1100	LHSV dropped to 0.9-1.0 to match available H ₂ flowrate.
6/1/80	1000	End test period 4.
	1000	Unit shut down because of further problems with hydrogen supply.

TABLE 3 (CONT'D)
CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
6/3/80	0100	Restart unit.
	0900	End lineout, start test period 5. Pressure still below desired 1250.
6/5/80	0100	End test period 5.
	0100	Start test period 6.
6/6/80	1300	End test period 6.
	1300	Start test period 7.
6/7/80	2300	End test period 7.
	2300	Start test period 8.
6/9/80	1300	End test period 8.
	1300	Start test period 9.
6/11/80	0300	End test period 9.
	0300	Start test period 10.
6/12/80	1900	End test period 10. Some inter- mittent feed problems.
	1900	Start test period 11. Intermit- tent feed problems.
6/14/80	1000	End test period 11.
	1000	Start test period 12.
6/15/80	2400	End test period 12.
	2400	Start test period 13.
6/17/80	1000	Hydrogen supply pressure problems corrected. Pressure, LHSV, H ₂ flow raised to design conditions.
	1400	End test period 13.
	1400	Start test period 14.
	1500	Feed pump down one hour.
6/19/80	0500	End test period 14.
	0500	Start test period 15.
6/20/80	1300	Feed pump down.
	1600	Feed pump repaired.
	2200	End test period 15.
	2200	Start test period 16.

TABLE 3 (CONT'D)
CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
6/22/80	1200 1200	End test period 16. Start test period 17.
6/24/80	0200 0200	End test period 17. Start test period 18.
6/25/80	1600 1600	End test period 18. Start test period 19.
6/27/80	0600 0600	End test period 19. Start test period 20.
6/28/80	2200 2200	End test period 20. Start test period 21.
6/30/80	1400 1400	End test period 21. Start test period 22.
7/2/80	0600 0600	End test period 22. Start test period 23.
7/3/80	0600	End test period 23. Unit shut down for scheduled catalyst change of guardbed and reactor and for required maintenance activities.
7/10/80		Load new guardbed catalyst and reactor catalyst.
7/15/80		Completed required maintenance and pressure checking activities.
7/16/80		Presulfide catalyst.
7/17/80	1300 2100 2100	Start lineout. End lineout. Start test period 24.
7/19/80	1300 1300	End test period 24. Start test period 25.
7/21/80	0500 0500	End test period 25. Start test period 26.

TABLE 3 (CONT'D)
CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
7/22/80	1300	Feed pump off one hour to relieve plugging problem.
	2200	End test period 26.
	2200	Start test period 27.
7/24/80	1400	End test period 27.
	1400	Start test period 28.
7/26/80	0600	End test period 28.
	0600	Start test period 29.
7/27/80	2200	End test period 29.
	2200	Start test period 30.
7/29/80	1400	End test period 30.
	1400	Start test period 31.
7/31/80	0600	End test period 31.
	0600	Start test period 32.
8/1/80	2200	End test period 32.
	2200	Start test period 33.
8/3/80	1400	End test period 33.
	1400	Start test period 34.
8/5/80	0600	End test period 34.
	0600	Start test period 35.
8/6/80	2200	End test period 35.
	2200	Start test period 36.
8/7/80	0800	End test period 36. Shut down unit for required maintenance and for changeout of guardbed catalyst.
8/8/80		Fresh charge of catalyst in guardbed.
8/9/80	1600	Start lineout period.
8/10/80	0100	End lineout.
	0100	Start test period 37.
8/11/80	1700	End test period 37.
	1700	Start test period 38.

TABLE 3 (CONT'D)

CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
8/13/80	0900	End test period 38.
	0900	Start test period 39.
8/15/80	0100	End test period 39.
	0100	Start test period 40.
8/16/80	1700	End test period 40.
	1700	Start test period 41.
8/18/80	0900	End test period 41.
	0900	Start test period 42.
8/20/80	0100	End test period 42.
	0100	Start test period 43.
8/21/80	0645	Feed pump off due to loss of plant hydrogen pressure.
	0930	Feed pump on, decrease feed rate.
	1900	End test period 43.
	1900	Start test period 44.
8/22/80	0830	Plant hydrogen problems; supply changed to lower pressure source. Decrease feed rate and system pressure.
8/23/80	0100	Feed pump off 30 minutes.
	1400	End test period 44.
	1400	Start test period 45.
8/25/80	0600	End test period 45.
	0600	Start test period 46.
8/26/80	2200	End test period 46.
	2200	Start test period 47.
	2200	Hydrogen supply pressures back to normal.
8/28/80	1400	End test period 47.
	1400	Start test period 48.
8/29/80	0700	End test period 48. Unit shut down for Labor Day weekend.

TABLE 3 (CONT'D)
CSHT RUN CHRONOLOGY

<u>Date</u>	<u>Time, Hrs.</u>	<u>Item</u>
9/2/80	1100 1900	Start lineout period. End lineout period. Start test period 49.
9/4/80	1100 1100 2200	End test period 49. Start test period 50. Feed pump off 30 minutes.
9/6/80	0300 0300	End test period 50. Start test period 51.
9/7/80	1900 1900	End test period 51. Start test period 52.
9/9/80	1100 1100	End test period 52. Start test period 53.
9/11/80	0300 0300	End test period 53. Start test period 54.
9/11/80	0700	End test period 54. Unit shut down.

TABLE 4
CRUDE SHALE HYDROTREATING

Period	4	5	6	7	8	9	10	11	12	13
OPERATING CONDITIONS										
Reactor Temperature, °F	685	693	681	678	680	681	681	678	678	679
Reactor LSHV, Hr ⁻¹	0.93	1.24	1.33	1.37	1.37	1.34	1.37	1.37	1.30	1.34
Pressure, PSIG	1110	1175	1175	1175	1175	1175	1175	1175	1175	1175
Gas Charge, SCFB	2460	3720	3700	3185	3590	3680	3580	3600	3801	3740
Hydrogen Content, Vol %	83.0	-	-	88.6	83.5	84.9	84.0	-	85.5	-
Guard Bed Temperature, °F	427	514	510	511	521	511	505	510	516	512
Guard Bed LHSV, Hr ⁻¹	1.90	2.53	2.71	2.79	2.79	2.73	2.79	2.79	2.31	2.73
COMBINED LIQUID PRODUCT INSPECTIONS										
API	28.2	27.8	27.7	27.6	27.8	27.7	27.9	27.8	27.9	28.2
Sulfur, Wt %	0.02	0.03	0.03	0.03	0.01	0.00	0.02	0.03	0.12	0.04
Nitrogen, Wt %	1.04	1.12	1.15	1.25	1.03	1.24	1.05	1.06	1.05	1.34
Basic Nitrogen, Wt %	0.73	0.65	0.79	0.79	0.79	0.79	0.80	0.79	0.79	0.81
Recovery, Wt %	99.1	99.8	96.8	98.6	96.6	99.8	96.0	97.7	98.9	99.2

TABLE 4 (CONT'D)
CRUDE SHALE HYDROTREATING

Period	14	15	16	17	18	19	20	21	22	23
OPERATING CONDITIONS										
Reactor Temperature, °F	677	678	677	678	677	677	681	678	686	675
Reactor LSHV, Hr ⁻¹	1.42	1.44	1.40	1.44	1.43	1.44	1.41	1.47	1.45	1.46
Pressure, PSIG	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Gas Charge, SCFB	3940	3900	4000	3860	3920	3810	3980	3810	3840	3830
Hydrogen Content, Vol %	82.9	78.5	79.4	-	80.9	78.7	-	-	76.6	79.3
Guard Bed Temperature, °F	504	510	514	526	527	525	526	525	520	527
Guard Bed LHSV, Hr ⁻¹	2.90	2.94	2.86	2.94	2.92	2.94	2.88	3.00	2.96	2.98
COMBINED LIQUID PRODUCT INSPECTIONS										
°API	28.1	28.3	28.4	28.2	27.9	27.8	27.7	27.9	27.9	28.0
Sulfur, Wt %	0.04	0.15	0.09	0.05	0.05	0.02	0.04	0.04	0.04	0.04
Nitrogen, Wt %	1.06	1.11	1.30	1.27	1.17	1.21	1.10	1.05	1.26	1.25
Basic Nitrogen, Wt %	0.80	0.80	0.80	0.79	0.83	0.82	0.81	0.79	0.82	0.81
Recovery, Wt %	97.2	99.0	97.8	98.6	98.7	99.1	100.4	93.1	98.7	98.1

TABLE 4 (CONT'D)
CRUDE SHALE HYDROTREATING

Period	24	25	26	27	28	29	30	31	32	33
OPERATING CONDITIONS										
Reactor Temperature, °F	680	680	679	676	679	680	679	680	679	680
Reactor LSHV, Hr ⁻¹	1.49	1.47	1.49	1.47	1.50	1.52	1.51	1.49	1.41	1.43
Pressure, PSIG	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Gas Charge, SCFB	3870	3930	3870	3930	3850	3800	3840	3880	4090	4040
Hydrogen Content, Vol %	73.7	72.8	86.7	-	-	-	74.1	79.1	76.9	76.8
Guard Bed Temperature, °F	510	526	516	510	509	595	510	501	508	519
Guard Bed LHSV, Hr ⁻¹	3.02	2.98	3.02	2.98	3.04	3.09	3.07	3.02	2.86	2.90
COMBINED LIQUID PRODUCT INSPECTIONS										
°API	28.2	28.2	28.4	27.9	28.3	28.1	28.1	28.0	27.3	27.6
Sulfur, Wt %	0.04	0.04	0.04	0.07	0.07	0.08	0.05	0.02	0.04	0.04
Nitrogen, Wt %	1.00	1.00	1.02	1.06	1.06	1.06	1.04	1.06	1.10	1.10
Basic Nitrogen, Wt %	0.78	0.82	0.72	0.78	0.84	0.81	0.77	0.79	0.81	0.78
Recovery, Wt %	98.8	99.9	101.0	98.7	98.6	97.8	98.7	98.5	94.5	99.8

TABLE 4 (CONT'D)

CRUDE SHALE HYDROTREATING

Period	34	35	36	37	38	39	40	41	42	43
OPERATING CONDITIONS										
Reactor Temperature, °F	681	682	685	679	682	682	681	681	685	684
Reactor LSHV, Hr ⁻¹	1.54	1.51	1.51	1.52	1.46	1.48	1.52	1.46	1.33	1.28
Pressure, PSIG	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Gas Charge, SCFB	3750	3840	3830	4000	4120	4160	4080	3960	3420	4030
Hydrogen Content, Vol %	77.3	82.1	-	77.9	77.1	74.5	77.9	-	72.2	-
Guard Bed Temperature, °F	551	541	468	501	510	511	509	499	518	531
Guard Bed LHSV, Hr ⁻¹	3.14	3.07	3.07	3.04	2.92	2.96	3.04	2.92	2.66	2.56
COMBINED LIQUID PRODUCT INSPECTIONS										
API	27.8	27.9	28.2	27.6	28.1	28.2	27.7	27.6	27.7	28.5
Sulfur, Wt %	0.05	0.09	0.04	0.02	0.08	-	0.08	0.09	0.09	0.07
Nitrogen, Wt %	1.13	1.11	1.10	1.12	1.08	1.11	1.10	1.10	1.04	1.18
Basic Nitrogen, Wt %	0.79	0.81	0.79	0.84	0.83	0.81	0.87	0.85	0.84	0.88
Recovery, Wt %	100.1	99.0	98.1	97.9	99.8	100.8	99.8	98.5	96.4	97.4

TABLE 4 (CONT'D)
CRUDE SHALE HYDROTREATING

Period	44	45	46	47	48	49	50	51	52	53
OPERATING CONDITIONS										
Reactor Temperature, °F	685	683	680	682	681	683	679	680	679	678
Reactor LSHV, Hr ⁻¹	1.28	1.32	1.50	1.47	1.64	1.49	1.47	1.47	1.42	1.45
Pressure, PSIG	1190	1165	1160	1235	1235	1230	1230	1230	1225	1240
Gas Charge, SCFB	4260	3540	3780	3920	3540	3600	3840	3660	4020	3930
Hydrogen Content, Vol %	-	71.8	65.7	64.3	64.7	60.8	59.2	60.8	59.8	59.8
Guard Bed Temperature, °F	321	513	501	505	505	535	532	536	551	541
Guard Bed LHSV, Hr ⁻¹	2.56	3.04	3.00	2.94	3.28	2.98	2.94	2.94	2.84	2.90
COMBINED LIQUID PRODUCT INSPECTIONS										
°API	28.1	27.6	27.5	27.7	27.7	27.3	27.6	27.3	27.9	28.5
Sulfur, Wt %	0.08	0.08	0.08	0.08	-	-	0.08*	-	-	-
Nitrogen, Wt %	1.45	1.45	1.10	1.38	-	-	1.12*	-	-	-
Basic Nitrogen, Wt %	0.86	0.88	0.88	0.87	-	-	0.88*	-	-	-
Recovery, Wt %	97.9	100.9	98.0	97.9	89.8	98.0	100.2	97.5	99.6	98.7

*Composite Analysis Only.

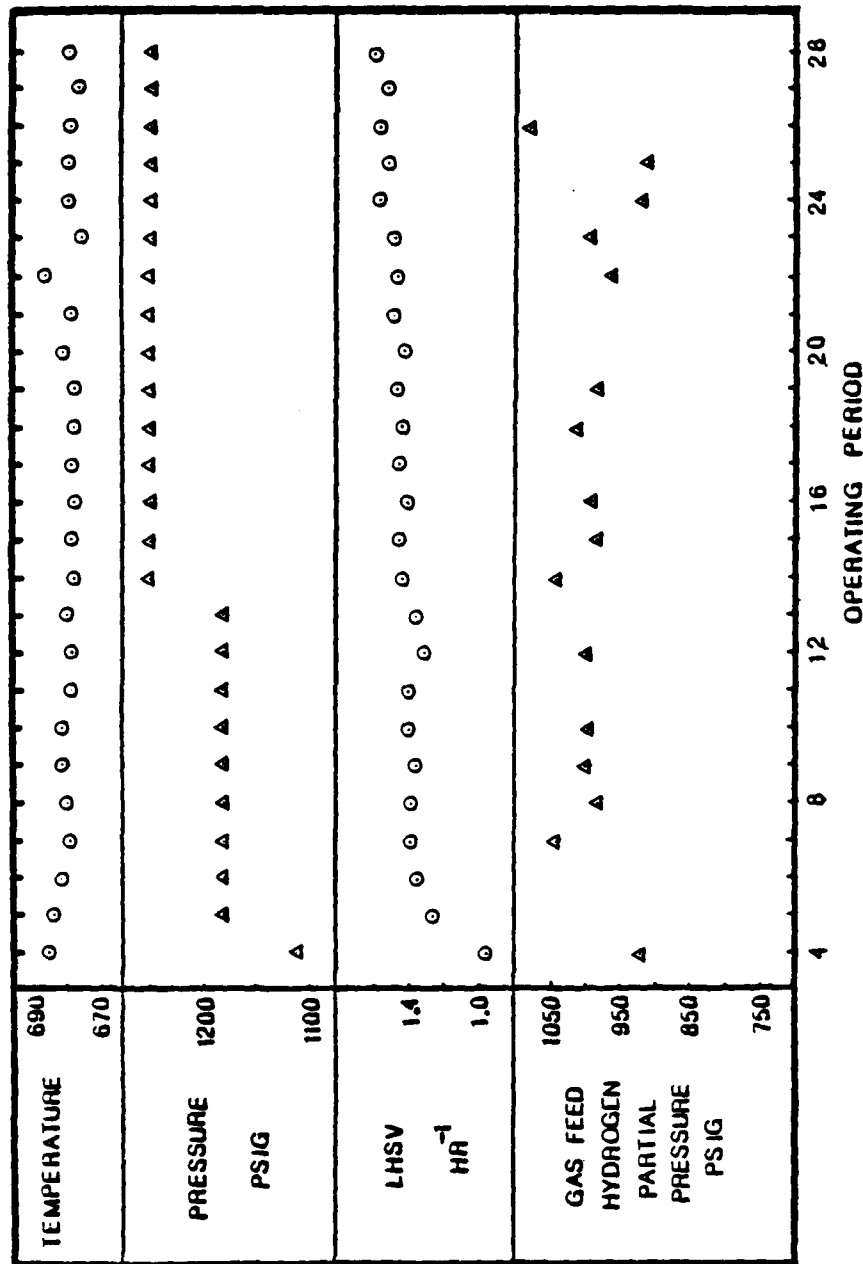


Figure 4. CSHT Operating Data And Results

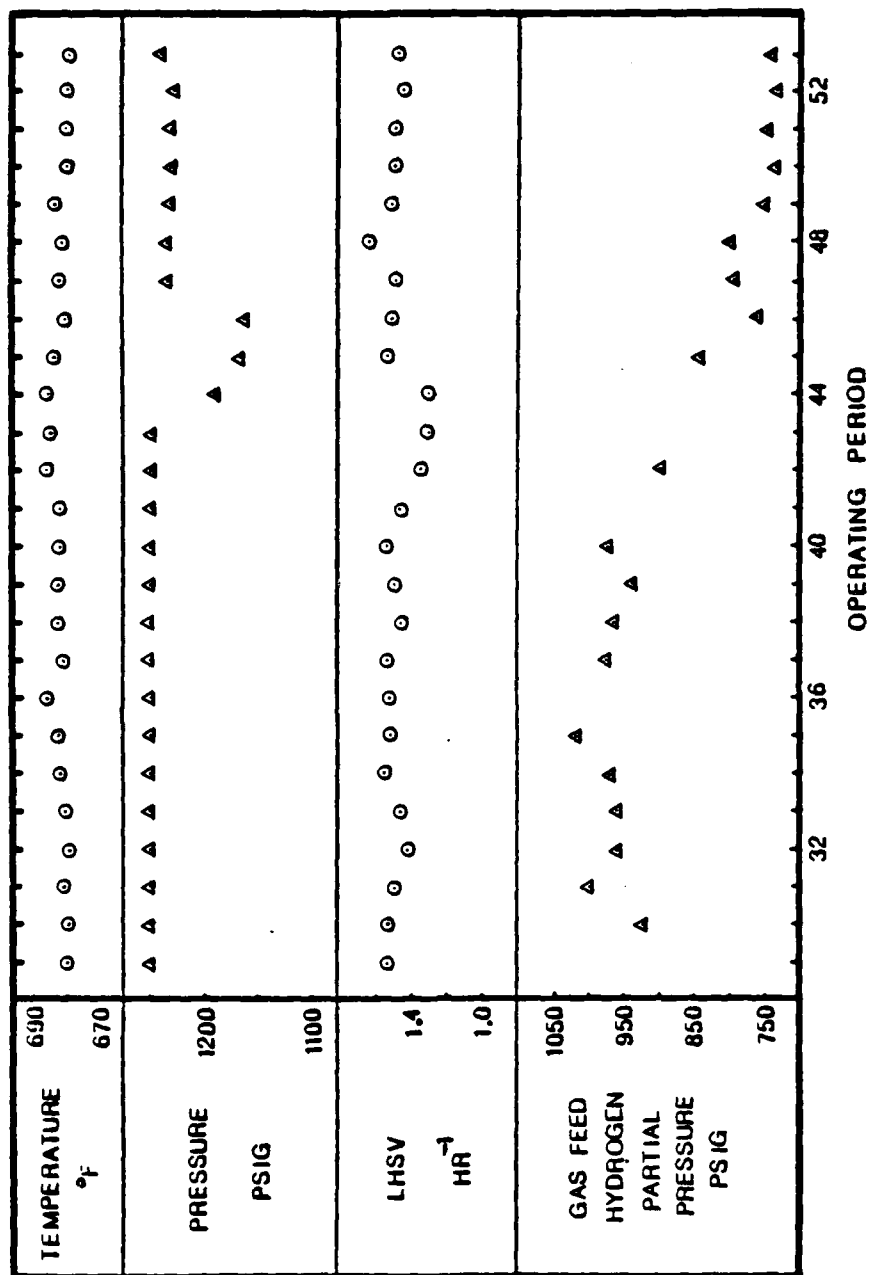


Figure 4 (Cont'd). CSHT Operating Data And Results

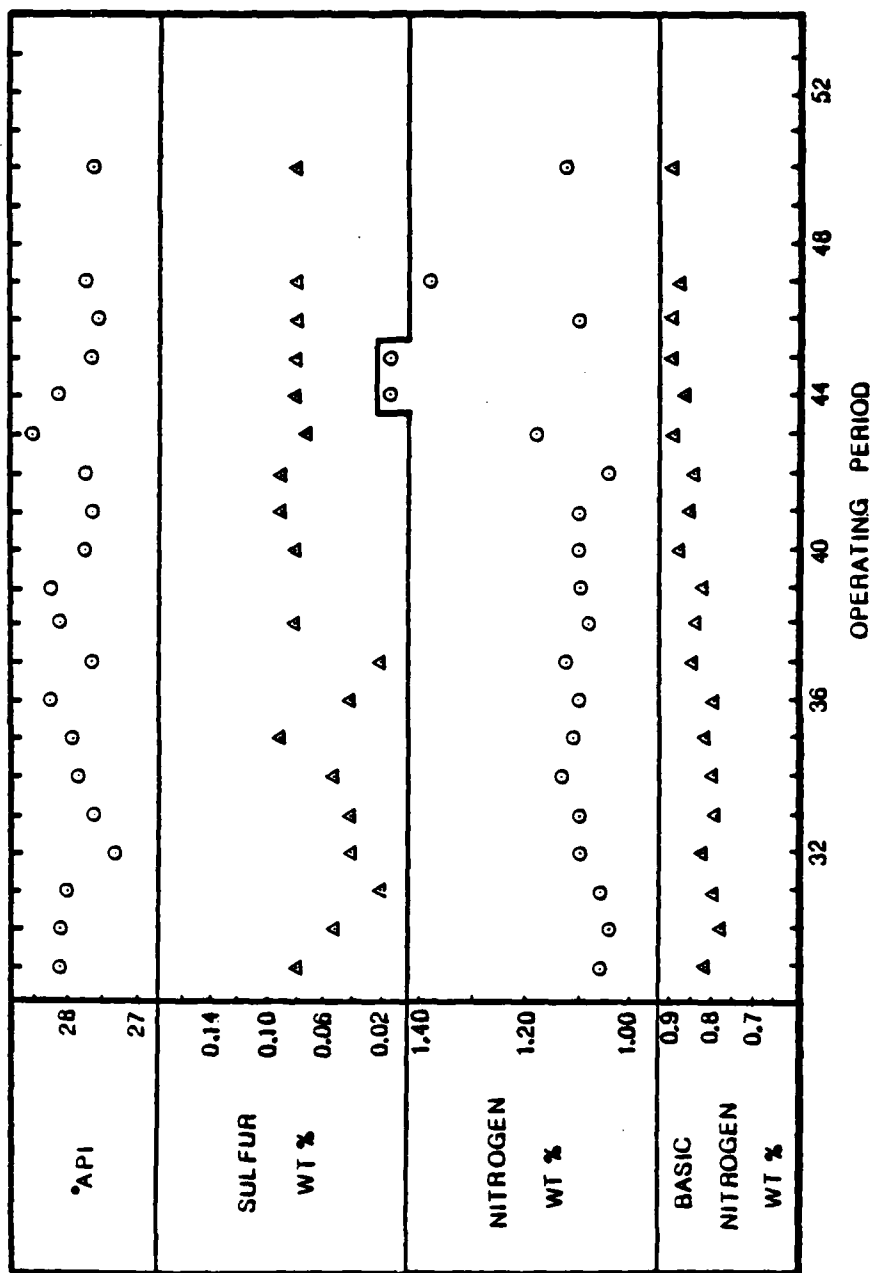


Figure 5 (Cont'd). CSHT Operating Data And Results

The slight variability of the composition of the refinery hydrogen source resulted in imposed variations in both the inlet and off-gas compositions of the crude shale oil hydrotreater which precluded material balance calculations for the individual operating periods. Material balances were computed for combined operating periods 4-23 and for combined operating periods 24-53 by using the inlet and off-gas compositions of individual operating periods as "point estimators" for the combined period average. The results of these balance calculations are shown in Tables 5 and 6, together with the properties of representative reaction product streams produced during the respective periods. Hydrogen contents of the liquid feedstock and product streams were employed to increase the accuracy of hydrogen consumption calculations. Yield structures for the combined periods, hydrogen and mass normalized to 100%, are given in Table 7.

The results obtained from the analysis of several samples of hydrotreater stripper overhead are given in Table 8. The analytical results for hydrotreater stripper bottom stream composites are shown in Table 9.

(Continued on page 41)

TABLE 5
GROSS BALANCE AND FRACTION DATA

MATERIAL BALANCE			
WT % FEED			
PERIODS COVERED	4 - 23		
FEED	100.00		
GAS CHARGE	23.35		
TOTAL CHARGE	123.35		
LIQUID RECOVERY	98.17		
GAS RECOVERY			
H ₂ - C ₅	25.94		
H ₂ O	0.75		
H ₂ S	0.64		
NH ₃	0.36		
TOTAL RECOVERY	125.86		
CLOSURE, WT %	102.0		
REPRESENTATIVE FRACTION PROPERTIES			
ITEM	STRIPPER OVERHEAD	DISTILLATION FRACTIONS	
		OVERHEAD	BOTTOMS
WT % FEED	10.3	25.7	60.7
°API	(41.0)	34.1	24.3
NITROGEN, WT %	0.88	0.97	1.06
BASIC NITROGEN, WT %	0.79	0.78	0.75
SULFUR, WT %	0.02	0.02	0.10
HYDROGEN, WT %	-	13.2	12.3
OXYGEN, WT %	0.31	0.27	0.22
RAMSBOTTOM CARBON	-	0.20	0.92
IRON, PPM	-	<1	28
NICKEL, PPM	-	<1	2
VANADIUM, PPM	-	<1	<1
ARSENIC PPM	-	<1	1
DISTILLATION, SIM-D, °F			
IBP	202	335	595
5 WT %	289	414	615
10 WT %	326	439	631
50 WT %	440	530	758
90 WT %	551	592	899
95 WT %	590	598	929
EP	816	629	948

TABLE 6

GROSS BALANCE AND FRACTION DATA

MATERIAL BALANCE			
WT % FEED			
PERIODS COVERED	24-53		
FEED	100.00		
GAS CHARGE	32.29		
TOTAL CHARGE	132.29		
LIQUID RECOVERY	98.71		
GAS RECOVERY			
H ₂ - C ₅	35.30		
H ₂ O	0.74		
H ₂ S	0.61		
NH ₃	0.36		
TOTAL RECOVERY	135.72		
CLOSURE, WT %	102.6		
REPRESENTATIVE FRACTION PROPERTIES			
ITEM	STRIPPER OVERHEAD	DISTILLATION FRACTIONS	
		OVERHEAD	BOTTOMS
WT % FEED	10.1	20.7	66.0
°API	(41.0)	34.1	23.6
NITROGEN, WT %	0.88	1.28	1.42
BASIC NITROGEN, WT %	0.79	0.84	0.73
SULFUR, WT %	0.01	0.03	0.10
HYDROGEN, WT %	-	13.0	12.1
OXYGEN, WT %	-	-	-
RAMSBOTTOM CARBON	-	0.17	0.67
IRON, PPM	-	<1	27
NICKEL, PPM	-	<1	3
VANADIUM, PPM	-	<1	<1
ARSENIC PPM	-	<1	1
DISTILLATION, SIM-D, °F			
IBP	191	334	577
5 WT %	289	410	599
10 WT %	324	433	613
50 WT %	435	522	750
90 WT %	546	582	910
95 WT %	587	588	941
EP	826	627	982

TABLE 7
CSHT YIELD STRUCTURE

(WT% FEED NORMALIZED TO 100%)

OPERATING PERIODS	4-23	24-53
(H ₂ O)	0.74	0.72
(H ₂ S)	0.67	0.59
(NH ₃)	0.35	0.35
H ₂	-1.11	-1.08
C ₁	0	0
C ₂	0	0.82
C ₃	0.83	1.68
C ₄	0.33	0.45
C ₅	1.59	0.87
STRIPPER OVERHEAD	8.25	10.62
FRACTIONATER OVERHEAD (<600°F)	26.30	21.10
FRACTIONATER BOTTOMS (>600°F)	62.06	63.89
HYDROGEN CONSUMPTION (SCFB)	665	646

TABLE 8
CSHT STRIPPER OVERHEAD INSPECTIONS

COMPOSITE NO.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CSHT PERIODS	3	8	13	18	22	30	38	43	48	53	-	-	-	-	-	-	-	-	-
*API *	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)	(41.0)
SULFUR, WT %	-	0.01	0.00	0.07	0.02	0.01	0.03	-	-	-	-	-	-	-	-	-	-	-	-
NITROGEN, WT %	-	0.91	0.78	0.88	0.88	0.88	0.97	-	-	-	-	-	-	-	-	-	-	-	-
BASIC NITROGEN, WT %	-	0.81	-	0.86	0.79	0.79	0.49	-	-	-	-	-	-	-	-	-	-	-	-
HYDROGEN, WT %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
OXYGEN, WT %	-	-	-	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IRON, PPM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NICKEL, PPM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
VANADIUM, PPM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ARSENIC, PPM	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RAMSBOTTOM CARBON, WT %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DISTILLATION, D2887(WT %)(°F)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IBP	172	204	194	210	202	191	189	202	227	92	-	-	-	-	-	-	-	-	-
5	263	285	284	294	289	289	297	293	308	297	-	-	-	-	-	-	-	-	-
10	291	317	318	331	326	324	333	328	343	329	-	-	-	-	-	-	-	-	-
50	402	425	426	446	440	435	447	438	454	444	-	-	-	-	-	-	-	-	-
90	510	535	533	558	551	546	565	559	579	563	-	-	-	-	-	-	-	-	-
95	562	679	572	594	590	587	604	603	642	609	-	-	-	-	-	-	-	-	-
EP	820	812	695	807	816	826	873	886	882	873	-	-	-	-	-	-	-	-	-
GROSS HEATING VALUE, BTU/LB	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AVERAGE WT % FEED	5.0	6.9	8.4	11.2	10.3	10.1	11.4	8.2	10.3	11.4	-	-	-	-	-	-	-	-	-

*Composite Value

TABLE 9
CSHT STRIPPER BOTTOMS COMPOSITES

COMPOSITE NO.	1	2	3	4	5	6	7	8	9	10
CSHT PERIODS	1-6	7-11	12-16	17-23	24-28	29-33	34-38	39-43	44-48	49-53
API	27.4	27.0	27.0	26.5	27.0	26.6	26.5	26.5	26.3	26.1
SULFUR, WT %	0.04	0.03	0.07	0.04	0.04	0.04	0.08	0.07	0.08	0.13
NITROGEN, WT %	1.20	1.32	1.33	1.16	1.03	1.15	1.13	1.39	1.46	1.13
BASIC NITROGEN, WT %	0.76	0.82	0.80	0.82	0.74	0.79	0.84	0.85	0.86	0.88
HYDROGEN, WT %	12.74	12.66	12.65	12.7	12.8	12.7	12.6	12.7	12.7	12.5
OXYGEN, WT %	0.23	0.24	0.22	0.24	0.30	0.31	0.35	0.29	0.30	0.30
IRON, PPM	3	9	8	9	6	8	12	6	11	-
NICKEL, PPM	1	1	1	2	1	2	2	2	2	-
VANADIUM, PPM	<1	<1	<1	<1	<1	<1	<1	<1	<1	-
ARSENIC, PPM	3	3	1	1	1	1	1	1	1	-
RAMSBOTTOM CARBON, WT %	0.52	0.53	0.61	0.64	0.54	0.60	0.58	0.58	0.72	0.55
DISTILLATION, D2887(WT %X°F)										
IBP	316	-	-	317	356	365	387	363	357	402
5	434	-	-	421	451	457	461	456	453	452
10	477	-	-	463	488	498	502	498	493	482
50	677	-	-	672	674	693	686	685	683	672
90	917	-	-	886	869	911	885	885	886	878
95	962	-	-	933	906	950	929	926	930	923
EP	1,009	-	-	992	941	999	971	964	964	971
GROSS HEATING VALUE, BTU/LB	19,294	19,152	19,119	19,122	19,094	19,064	19,036	19,017	19,026	19,099
AVERAGE WT % FEED	95.0	91.4	88.9	88.1	89.7	88.8	88.3	87.2	87.4	87.6

Tables 10 and 11 show the results of the analyses of the <600°F overhead and >600°F bottoms stream composites obtained from fractionation of the hydrotreater stripper bottoms. Because of mixing which occurred in fractionation, and because of sample compositing, correspondence of properties is limited to groups of CSHT operating periods as indicated. The yields listed as the "average weight percent of feed" for these streams are recovered yields, and reflect handling and fractionation losses.

It should be noted that the data listed in Tables 4, 8, 9, 10, and 11 reflect separate analytical determinations, and that the analytical problems cited previously are reflected in the data for nitrogen and sulfur. It should be further noted that the iron levels cited in Tables 9, 10, and 11 probably result from contamination in handling and fractionation, and do not necessarily reflect reactor exit iron levels.

Catalysts from both the hydrotreating and guardbeds were removed in sections during bed changes and at the termination of the operation. Samples of these catalysts were subjected to physical and chemical examination, and the results of the examination of the catalysts used in operating periods 4-53 are shown in Table 12. The calculated bed average properties for the regenerated hydrotreater catalysts from periods 1-53 are listed in Table 13 and plotted in Figure 6 as a function of total stream time. A correlation of regenerated surface area (% original surface area)

(Continued on page 47)

TABLE 10
CSHT FRACTIONATOR OVERHEAD COMPOSITES

COMPOSITE NO.	1	2	3	4	5
CSHT PERIODS	1-23	1-23	24-34	35-44	45-53
^o API	34.8	34.1	34.2	34.1	33.9
SULFUR, WT %	0.02	0.02	0.02	0.03	0.05
NITROGEN, WT %	0.89	0.97	1.31	1.28	1.34
BASIC NITROGEN, WT %	0.72	0.78		0.84	0.88
HYDROGEN, WT %	13.2	13.2	12.9	13.0	13.0
OXYGEN, WT %	0.25	0.27	-	-	-
IRON, PPM	<1	<1	1	<1	<1
NICKEL, PPM	<1	<1	<1	<1	<1
VANADIUM, PPM	<1	<1	<1	<1	<1
ARSENIC, PPM	<1	<1	<1	<1	<1
RAMSBOTTOM CARBON, WT %	0.21	0.20	0.13	0.17	0.14
DISTILLATION, D2887(WT%N°F)					
IBP	310	335	340	334	314
5	335	414	410	410	405
10	428	439	431	433	430
50	527	530	521	522	521
90	591	592	583	582	579
95	600	598	593	588	583
EP	629	629	619	627	614
GROSS HEATING VALUE, BTU/LB	19,216	19,203	20,745	19,258	19,207
AVERAGE WT % FEED	25.7	25.7	23.1	20.7	21.0

TABLE 11
CSHT FRACTIONATOR BOTTOMS COMPOSITES

COMPOSITE NO.	1	2	3	4	5	6	7	8	9
CSHT PERIODS	1-23	1-23	1-23	24-34	24-34	35-44	35-44	45-53	45-53
°API	24.2	24.0	24.3	23.4	23.3	23.6	23.6	23.9	24.0
SULFUR, WT %	0.09	0.10	0.10	0.09	0.09	0.10	0.09	0.11	0.11
NITROGEN, WT %	1.02	1.01	1.06	1.38	1.42	1.42	1.37	1.46	1.46
BASIC NITROGEN, WT %	0.72	0.75	0.75	0.76	0.77	0.73	0.77	0.80	0.80
HYDROGEN, WT %	12.2	12.2	12.3	12.0	11.9	12.1	12.1	-	-
OXYGEN, WT %	0.22	0.21	0.22	-	-	-	-	-	-
IRON, PPM	28	19	28	26	26	27	20	20	22
NICKEL, PPM	2	2	2	3	3	3	3	3	2
VANADIUM, PPM	<1	<1	<1	<1	<1	<1	1	1	1
ARSENIC, PPM	1	2	1	1	1	1	1	2	2
RAMSBOTTOM CARBON, WT %	0.94	0.87	0.92	0.72	0.70	0.67	-	0.59	0.71
DISTILLATION, D2887(WT %X°F)									
IBP	595	599	595	591	587	577	577	584	579
5	618	622	615	608	605	599	606	604	597
10	633	636	631	624	625	613	618	621	613
50	756	767	758	763	755	750	747	756	755
90	896	932	899	931	901	910	894	915	924
95	926	959	929	960	930	941	927	941	955
EP	946	984	948	982	950	982	950	984	1,015
GROSS HEATING VALUE, BTU/LB	19,103	19,102	19,040	18,996	19,051	19,082	19,061	19,038	19,007
AVERAGE WT % FEED	60.7	60.7	60.7	64.8	64.8	66.0	66.0	66.8	66.8

TABLE 12
CSHT CATALYST PROPERTIES

SAMPLE OBTAINED FROM TIME ON CATALYST, HR	REACTOR				GUARD BED				REACTOR				GUARD BED			
	789				910				1176				500			
	4-23				1-23				24-54				24-36			
LOCATION IN CATALYST BED	TOP	MID	BTM	TOP	MID	BTM	TOP	MID	BTM	TOP	MID	BTM	TOP	MID	TOP	MID
CONTAMINANTS																
CARBON, WT %	16.32	18.92	17.94	22.06	22.80	23.54	16.30	17.70	14.96	12.96	21.75	19.37				
IRON, WT %	6.66	1.82	1.04	0.63	1.66	0.56	9.10	4.23	0.22	0.15	0.10	0.01				
ARSENIC, WT %	2.69	0.49	0.30	0.62	0.22	0.08	1.14	0.62	<0.01	<0.01	1.08	0.11				
SPENT CATALYST PHYSICALS																
SURFACE AREA, M ² /GM	29	68	122	1	1	3	24	68	0.5	2	<1	2				
H ₂ PORE VOL. (<6000 Å), CM ³ /GM	0.08	0.13	0.14	0.02	0.01	0.02	0.08	0.14	0.05	0.04	0.02	0.04				
H ₂ PORE VOL. (TOTAL), CM ³ /GM	0.09	0.13	0.14	0.05	0.04	0.03	0.08	0.14	0.08	0.06	0.04	0.07				
REGENERATED CATALYST PHYSICALS																
SURFACE AREA, M ² /GM	104	172	202	204	224	228	80	166	262	262	235	218				
H ₂ PORE VOL. (<6000 Å), CM ³ /GM	0.25	0.45	0.54	0.15	0.18	0.17	0.19	0.41	0.18	0.19	0.17	0.22				
H ₂ PORE VOL. (TOTAL), CM ³ /GM	0.26	0.46	0.54	0.25	0.27	0.25	0.20	0.41	0.23	0.25	0.23	0.27				

TABLE 13

REGENERATED CSHT CATALYSTS:
CALCULATED BED AVERAGE
CONTAMINANT LEVELS

Stream Time (hr)	0	122	789	1176
(Fe + As) Wt. %	0	0.54	4.43	5.70
Surface Area as % of Original Value	100	93.7	71.9	66.1
Pore Volume as % of Original Value	100	94.2	80.8	73.1

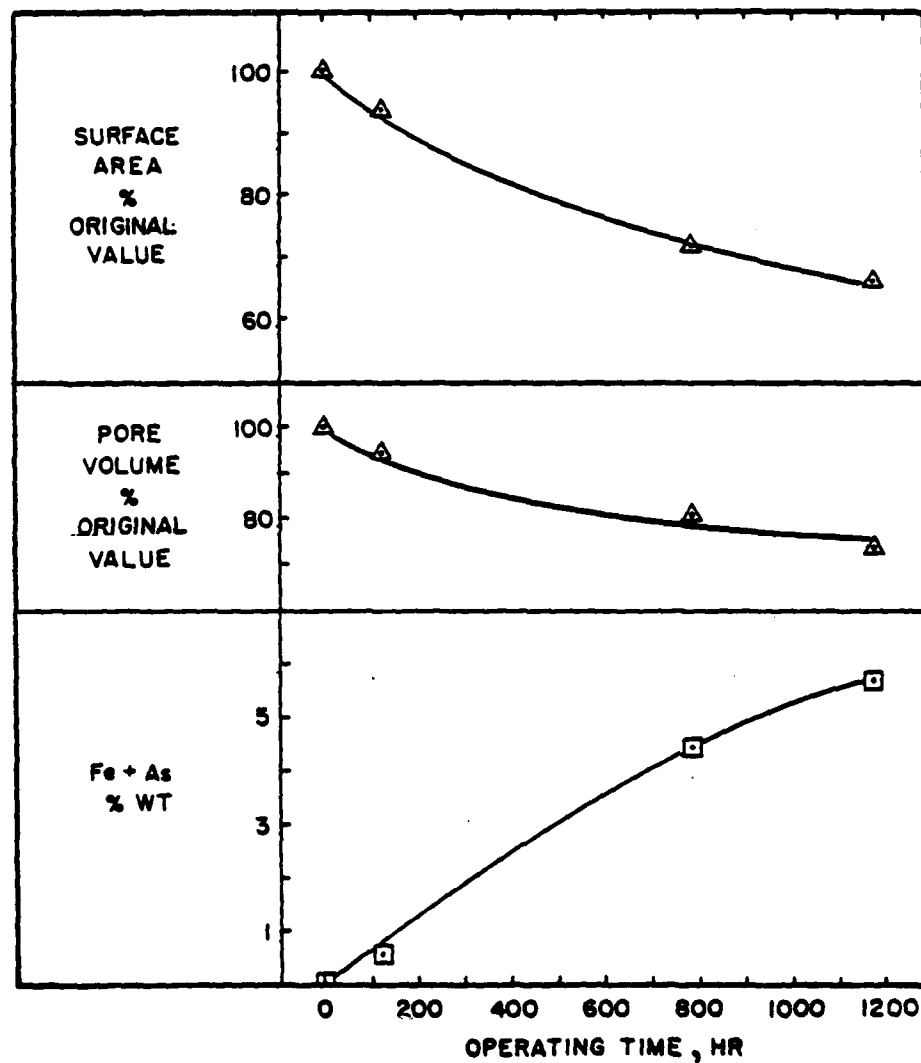


Figure 6. Properties Of Regenerated CSHT Reactor Catalyst

with metallic contamination is shown in Figure 7. A material accounting summary for this operation will be found in Section XI, Table 59.

7. CATALYST AGING

The results obtained during operating periods 24-53 were selected to estimate catalyst life because of the length of the run, the relative stability of hydrotreater operation, and the common analytical procedure used to determine nitrogen levels in the feed and reactor product streams. Results obtained during operating periods 44-47 were eliminated from analysis because of hydrogen supply pressure problems. Total nitrogen content was selected as the basis variable for estimation of catalyst life, and inspection of the data indicated that catalyst equilibration was attained after approximately 500 hours on stream. Regression analysis of the data after this time yielded the following equation:

$$\% N_t = 1.08 + 4.19 \times 10^{-5} \text{ Time (hr)}$$

This equation would predict a zero activity (1.4% effluent nitrogen) in 320 days on a linear basis, or an increase of 0.18% N_t in six months. Use of the nitrogen model developed in Phase II work with Co/Mo hydrotreating catalysts indicates that reasonable activity can be maintained for one year if a 0.2°F/day temperature increase is maintained throughout the cycle.

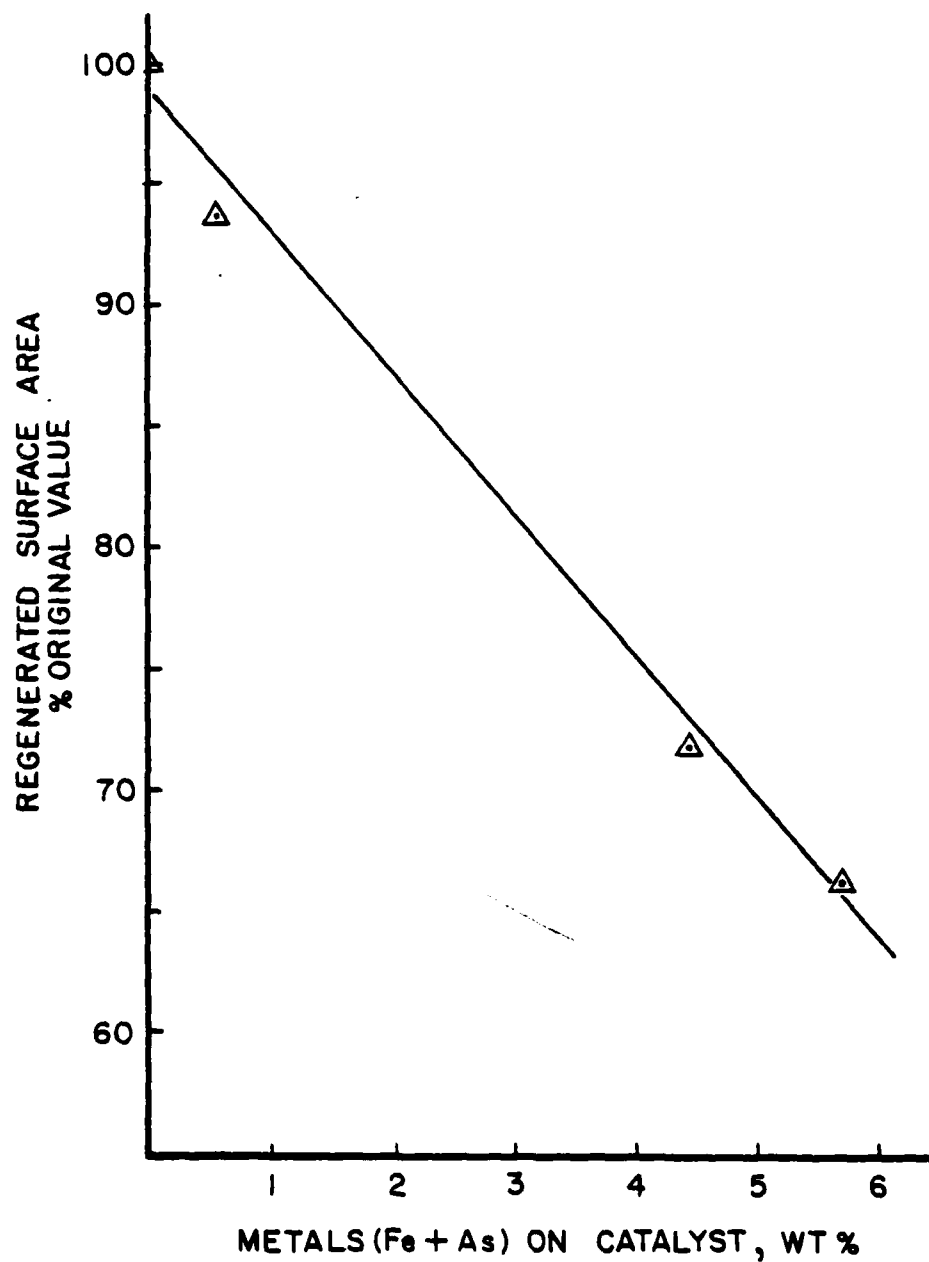


Figure 7. Effect Of Metals On CSHT Catalyst Regeneration

This estimate of a one-year catalyst life cycle is, in all probability, a conservative minimum because of the following reasons:

- A. The catalyst was severely fouled with arsenic and iron because of the inefficiency of the guardbed as indicated in Table 12 and Figures 6 and 7. The loss of pore volume and surface area explain much of the loss of denitrogenation activity observed.
- B. The decrease in hydrogen partial pressure during the latter stages of the run also impact on the denitrogenation activity shown.

8. DISCUSSION

The results obtained indicate that crude shale hydro-treating at low severity conditions provided an excellent method for preparing crude shale for subsequent processing in spite of the marginal performance of the guardbed in removing metallic contaminants. The low hydrogen consumption, and the excellent desulfurization levels are shown together with minimum nitrogen removal. The intended and observed increase in the ratio of basic-to-total nitrogen shown in the comparison of the feeds and full range products contributes to the economic advantages of the EXTRACTACRACKING process by reducing overall hydrogen requirements, while preparing the feedstock for subsequent acid extraction.

The relative inefficiency of the activated alumina guardbed argues for its replacement with a hydrotreating catalyst as has been discussed in recent literature*. Catalyst life cycles, significantly longer than predicted by this study, would be expected in the absence of metallic fouling by arsenic and tramp metals.

*P.F. Lovell, M.G. Fryback, H.E. Reif, and J.P. Schwedock,
"Maximize Shale Oil Gasoline", Hydrocarbon Processing,
May 81, pp. 125-130.

SECTION IV
MODIFIED REDUCED CRUDE CONVERSION

1. OBJECTIVES

A key element in the EXTRACTACRACKING process is the application of modified reduced crude conversion technology to feedstocks high in nitrogen, particularly basic nitrogen, content. The primary objective of this operation is to cascade* an economic maximum of gas oil and heavier components into the jet fuel, diesel, and gasoline boiling ranges. Secondary, though economically important objectives of this operation are the reduction of sulfur and nitrogen levels, and redistribution of the hydrogen already available in the heavier shale fractions without external hydrogen addition.

2. MECHANICAL DESCRIPTION

The reactor used in this operation was a 0.25 B/D miniature version of a full scale fluid catalytic cracking unit, and which included features which made it, effectively, a modified reduced crude converter**. Specific details of the unit are proprietary, but, in general, the unit was composed of a riser, a spent catalyst disengaging and stripping

* A concept pioneered by Ashland Oil. Also, a mechanism which tends to predominate when using a cracking catalyst in the presence of considerable nitrogen.

**Ashland Oil's Reduced Crude Conversion Process, U.S. Patent No. 4,299,687 (Oct. 1981)

section, regenerator system, and regenerated catalyst standpipe. Regenerated catalyst was metered to the riser where it was mixed with oil feed by means of a slide valve. The catalyst-oil mixture flowed, in dilute phase, to the catalyst vented riser disengaging section*, where the spent catalyst and product vapors were separated, stopping the reaction. The residual oil content of the spent catalyst was reduced in the stripping section, and the stripped catalyst flowed into the regenerator. The carbon content of the stripped, spent catalyst was removed by air combustion in the regenerator system, and the regenerated catalyst flowed into the regenerated catalyst standpipe for reuse.

Catalyst inventory and circulation rates were such that the unit could be operated over varying time periods. Because of its small size, the unit was not heat balanced and was provided with external electric resistance heaters operating on automatic temperature control. Condensable product vapors were collected for fractionation in the off-line fractionator previously shown in Figure 3. Overheads (<600°F) were collected for acid extraction while the 600°F bottoms were used in further MRCC operations. All flows were measured to provide material balances and control for

*Ashland Oil's patented disengagement system, U.S. Patents 4,066,533 (Jan. 1978) and 4,070,159 (Jan. 1978).

the system. Non-condensed product gas composition, regenerator flue gas composition, and carbon contents of the spent and regenerated catalysts were also monitored for material balance purposes.

3. FEEDSTOCKS

The feedstocks which were employed in modified reduced crude conversion operations during Phase III are given in Table 14. Also indicated in this table are the approximate operating period groups of the CSHT operation present in the feeds. Physical and chemical inspections of composite samples of the feedstocks for the several MRCC runs are shown in Table 15. The virgin >600°F CSHT fractionator bottoms used in MRCC runs 1 and 7 is considered the base feedstock for comparison purposes. The feedstock for MRCC run 2 consisted of the stated blend of virgin CSHT fractionator bottoms with fractionator bottoms from MRCC run 1, which had been hydrotreated (COHT) as discussed in Section VI. The feed for MRCC run 3 was the stated admixture of virgin CSHT fractionator bottoms with fractionator bottoms from MRCC run 2. The feedstock for MRCC run 5 consisted of virgin CSHT fractionator bottoms, together with 5% (weight) extract obtained in the acid extraction operation to be covered in Section V. MRCC run 6 feedstock consisted of the fractionator bottoms from MRCC run 3, and the feedstock for MRCC run 8 comprised the >600°F fractionator bottoms from runs 3, 4, 5, 6, and 7.

TABLE 14
MRCC FEED BLENDS

MRCC NO.	WT % OF >600°F FRACTION FROM:				CSHT RUN PERIODS INCLUDED
	CSHT	COHT	MRCC RECYCLE	ACID EXTRACT	
1	100	0	0	0	1-3, 4-13, 14-23
2	60	40	0	0	1-3, 4-13, 14-23, 24-36
3	60	0	40	0	1-3, 4-13, 14-23, 24-36, 37-53
4	0	100	0	0	1-3, 4-13, 14-23
5	95	0	0	5	37-53
6	0	0	100	0	1-3, 4-13, 14-23, 24-36, 37-53
7	100	0	0	0	37-53
8	0	0	100	0	1-3, 4-13, 14-23, 24-36, 37-53

TABLE 15

[illegible]

TABLE 15 (CONT'D)
MRCC FEED COMPOSITE PROPERTIES

MRCC RUN NO.	5	6	7	7	8	8	8
COMPOSITE NO.	1	1	1	2	1	2	3
°API	23.1	23.6	23.9	24.0	22.1	21.3	21.5
SULFUR, WT %	0.09	0.06	0.10	0.11	0.07	0.07	0.06
NITROGEN, WT %	1.42	0.54	1.46	1.46	0.71	0.62	0.78
BASIC NITROGEN, WT %	1.10	0.36	0.80	0.80	0.27	0.21	0.30
HYDROGEN, WT %	-	-	-	-	11.7	11.6	11.4
OXYGEN, WT %	-	-	-	-	-	-	-
IRON, PPM	15	1	20	22	4	3	4
NICKEL, PPM	2	<1	3	2	<1	<1	<1
VANADIUM, PPM	<1	<1	1	1	1	1	1
ARSENIC, PPM	<1	<1	2	2	<1	<1	<1
RAMSBOTTOM CARBON, WT %	0.70	0.60	0.59	0.71	0.77	0.85	0.68
DISTILLATION, D2887(WT%K°F)							
IBP.	406	599	584	579	583	457	430
5	556	615	604	597	612	614	596
10	604	627	621	613	627	627	609
50	745	714	756	755	712	707	701
90	914	858	915	924	868	855	869
95	947	892	941	955	919	893	917
EP	992	943	984	1,015	1,014	947	1,001
GROSS HEATING VALUE, BTU/LB	-	19,036	19,038	19,007	19,000	18,887	19,108
AVERAGE WT % FEED	100	100	100	100	100	100	100

4. EXPERIMENTAL/RESULTS

The catalyst consisted of a specially chosen equilibrium catalyst obtained from Ashland's operations. Additional quantities of this catalyst were charged, as required, to maintain inventory during the MRCC operations.

Operations were relatively smooth considering the six-month duration of the runs. Occasional pump and plugging problems were corrected with minimum operational interruption.

The length of a given operating period was determined by the time required to collect a drum of liquid product. Gas samples were collected at eight-hour intervals from the reactor product gas and regenerator flue gas streams and analyzed for material balance purposes. Feedstock and liquid product weights, and all temperatures and flows were measured continuously and recorded hourly. Samples of the liquid product from each operating period were characterized for gravity and distillation. A summary of the operating conditions, yield structure, and physical properties obtained during the operating periods is shown in Table 16. The temperature cited is the average riser temperature. Conversions are shown both as observed, and corrected for the presence of <600°F components present in the feedstocks. Yield structures are normalized to 100% feed basis. Graphical presentation of these conditions and results is shown in Figures 8 to 15 for the various MRCC runs.

(Continued on page 79)

TABLE 16

(a) As Observed / Corrected For $< 600^{\circ}\text{F}$ In Feed (b) Normalized To 100%

TABLE 16 (CONT'D)

(a) As Observed / Corrected For $< 600^{\circ}\text{F}$ In Feed (b) Normalized To 100 %

TABLE 16 (CONT'D)

(a) As Observed / Corrected For $< 600^{\circ}\text{F}$ In Feed (b) Normalized To 100 %

TABLE 16 (CONT'D)

SUMMARY OF MRCC OPERATING PERIODS

MRCC Run Number	3	3	3	3	4	4	4	5	6	6	6	7
Operating Period Number	9	10	11		1	2		1	1	2	3	1
Operating Conditions												
Temperature, °F	1025	1025	1035	1035	1045	1035	1035	1035	1030	1035	1045	1085
Catalyst/Oil Ratio	4.5	5.4	4.5		3.6	4.5		5.0	5.0	4.6	3.3	4.0
Conversion, Wt % ^a (600°F Cut)	48.4/46.8	49.0/47.3	54.0/52.6	68.2/65.4	61.2/57.7	44.0/37.8	40.2/39.7	43.4/42.9	45.6/45.2	57.9/57.3	92.8	
Closure, Wt %	99.2	96.9	97.1		96.5	94.0		92.1	98.6	96.5	98.8	
Product Yields, Wt % Feed ^b												
H ₂	0.16	0.17	0.19	0.13	0.14	0.14	0.09	0.10	0.11	0.11	0.11	0.17
C ₁	0.92	0.98	0.88	0.64	0.58	0.70	0.46	0.48	0.84	1.52	2.85	
C ₂	1.60	1.87	1.61	1.11	1.02	1.37	0.75	0.77	1.53	2.85	3.51	
C ₃	2.61	2.80	2.88	3.96	3.54	1.83	1.81	1.93	2.38	3.51	2.34	
C ₄	2.12	2.20	2.49	3.53	3.33	1.32	1.81	2.00	1.91	2.34	40.14	
C ₅ - 600 °F	33.99	33.13	37.47	49.02	44.50	29.16	26.75	30.15	30.46	54.39	42.11	
+ 600 °F	51.59	51.05	45.98	31.83	38.81	56.00	59.84	56.63	7.92	8.37	7.36	
Coke	7.01	7.80	8.50	9.78	8.07	9.53	8.47					
Liquid Properties												
°API	28.4	28.0	28.7	32.3	31.4	26.9	26.7	26.5	26.7	28.6		
Distillation, °F, D2887												
IBP	91	107	98	69	85	154	110	113	110	110	110	
5 Wt %	207	221	207	157	182	281	233	230	222	207	207	
10 "	283	288	259	200	236	360	297	289	286	257	257	
30 "	553	550	475	336	436	593	611	588	568	452	452	
50 "	651	653	632	537	628	663	661	657	653	617	617	
70 "	722	728	704	657	694	746	720	718	716	700	700	
90 "	833	838	816	780	810	851	825	818	824	825	825	
95 Wt %	880	883	860	838	861	888	872	862	875	874	874	
EP	971	957	931	932	946	943	948	939	968	944	944	

(a) As Observed/Corrected For < 600°F in Feed (b) Normalized To 100%

SUMMARY OF MRCC OPERATING PERIODS

(c) As Observed / Corrected For $< 600^{\circ}\text{F}$ In Feed (b) Normalized To 100%

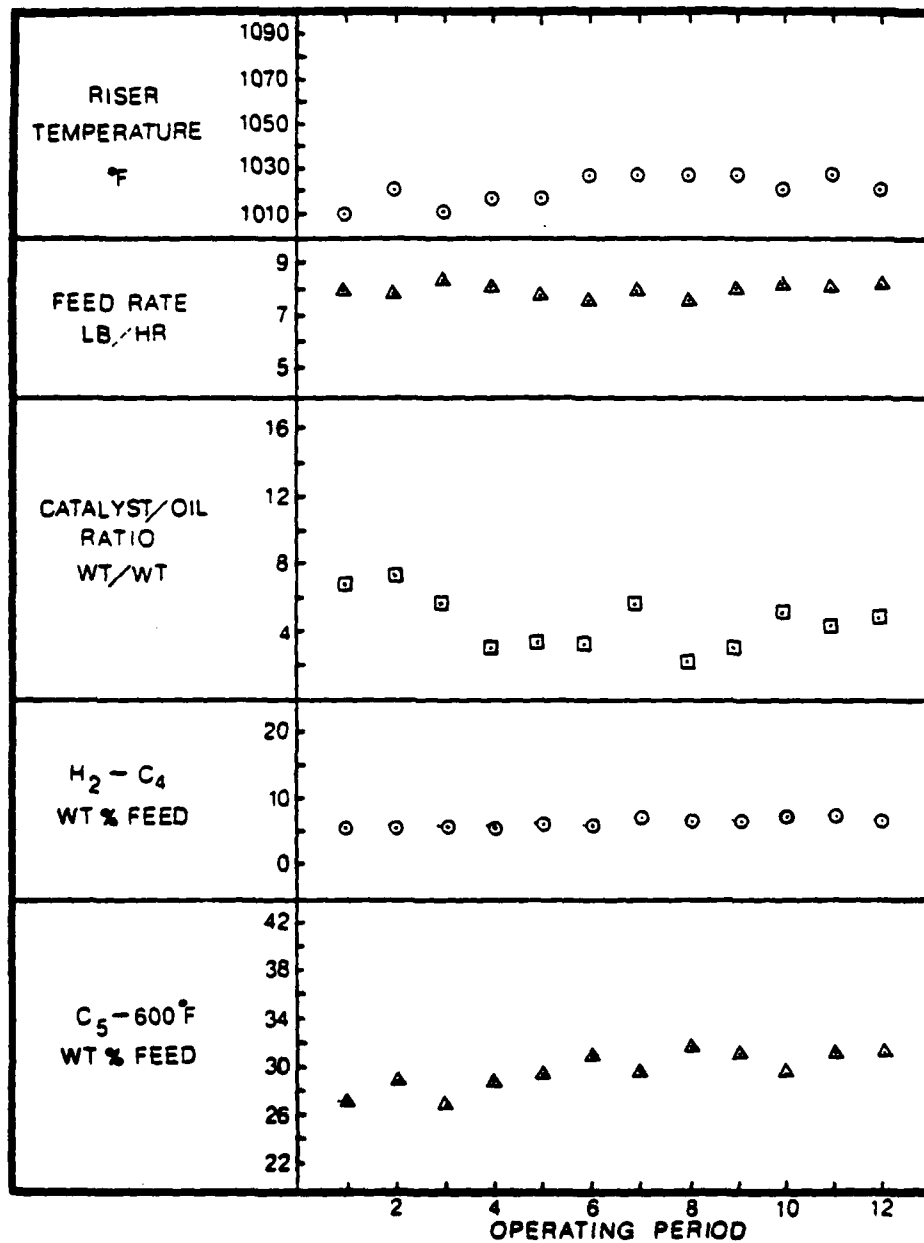


Figure 8. MRCC Run-1 Operating Conditions And Results

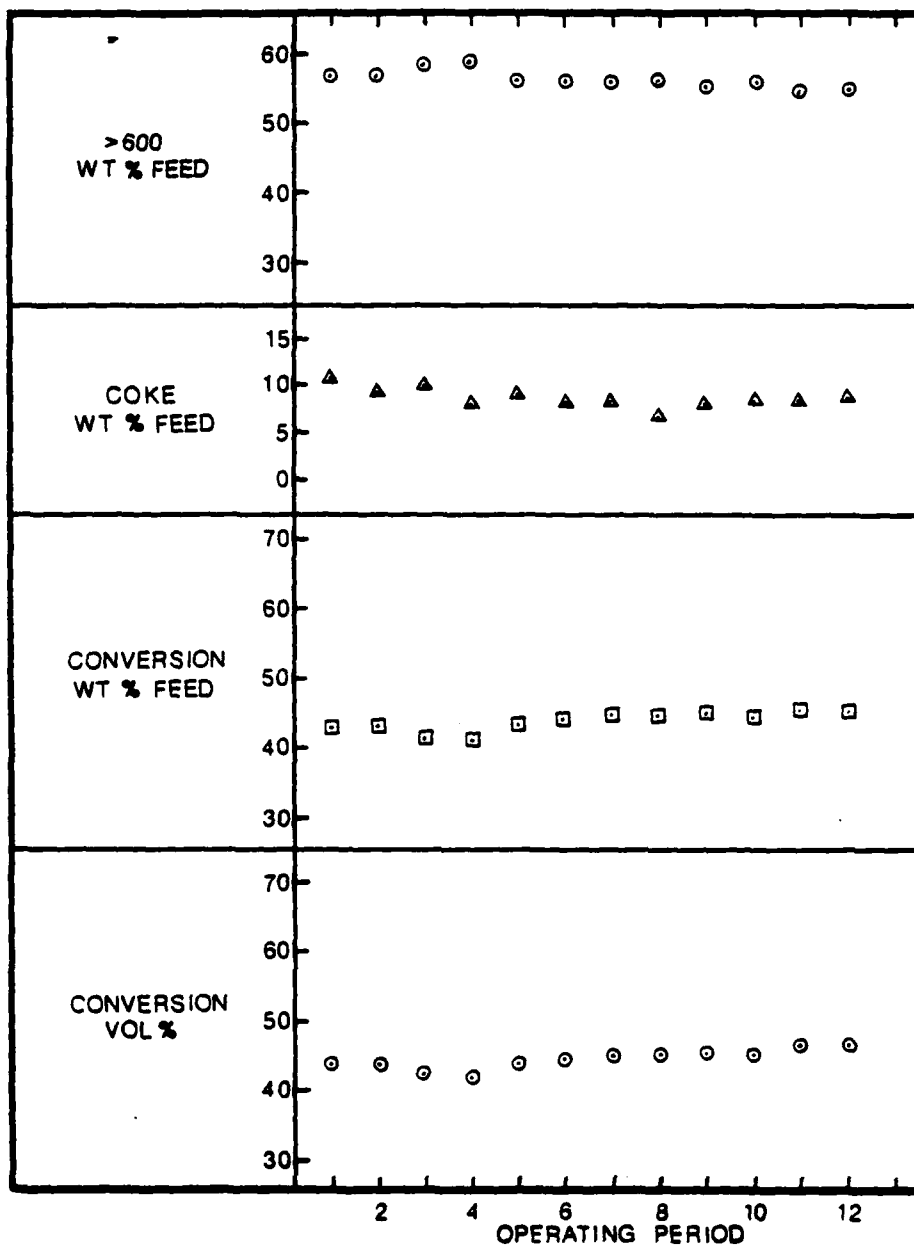


Figure 8 (Cont'd). MRCC Run-1 Operating Conditions And Results

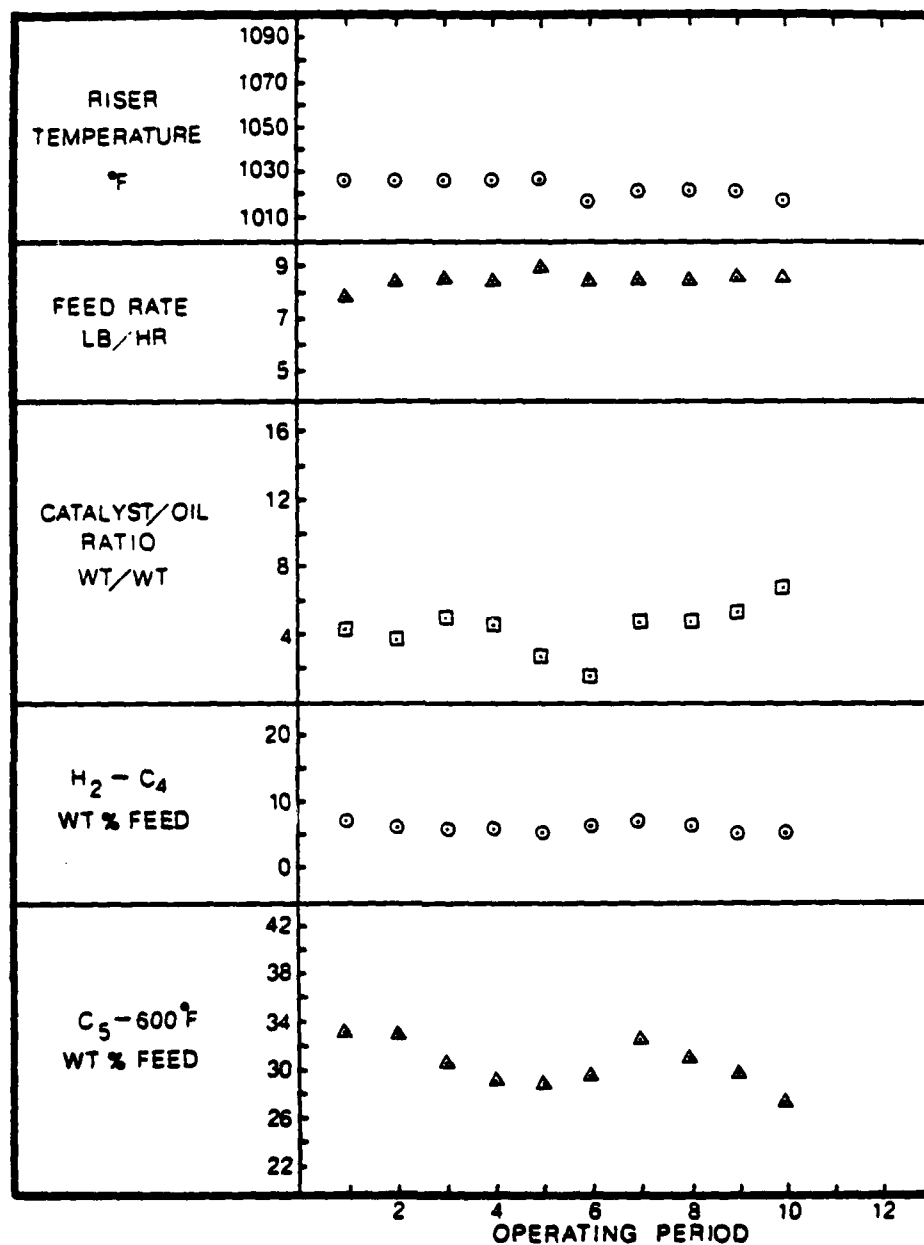


Figure 9. MRCC Run-2 Operating Conditions And Results

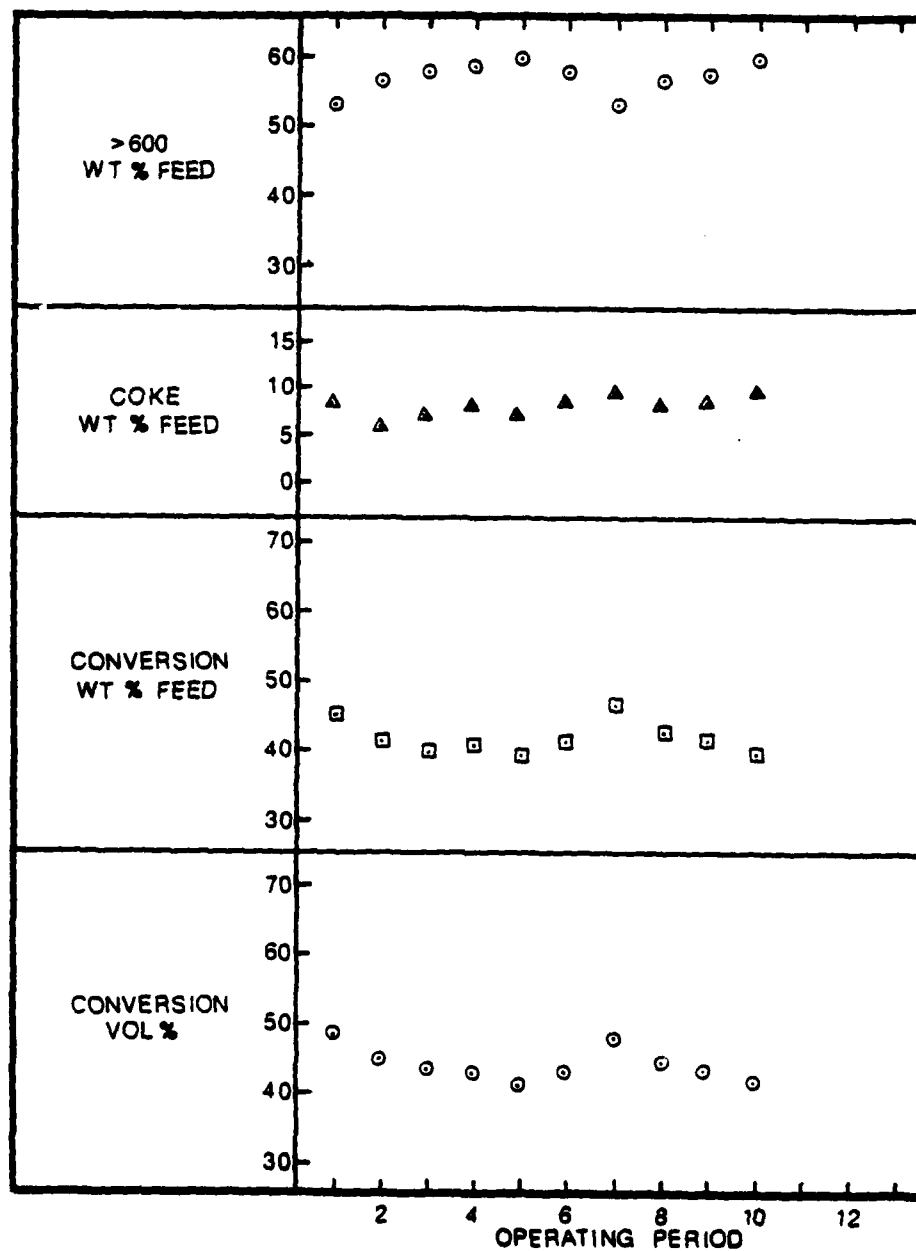


Figure 9 (Cont'd). MRCC Run-2 Operating Conditions And Results

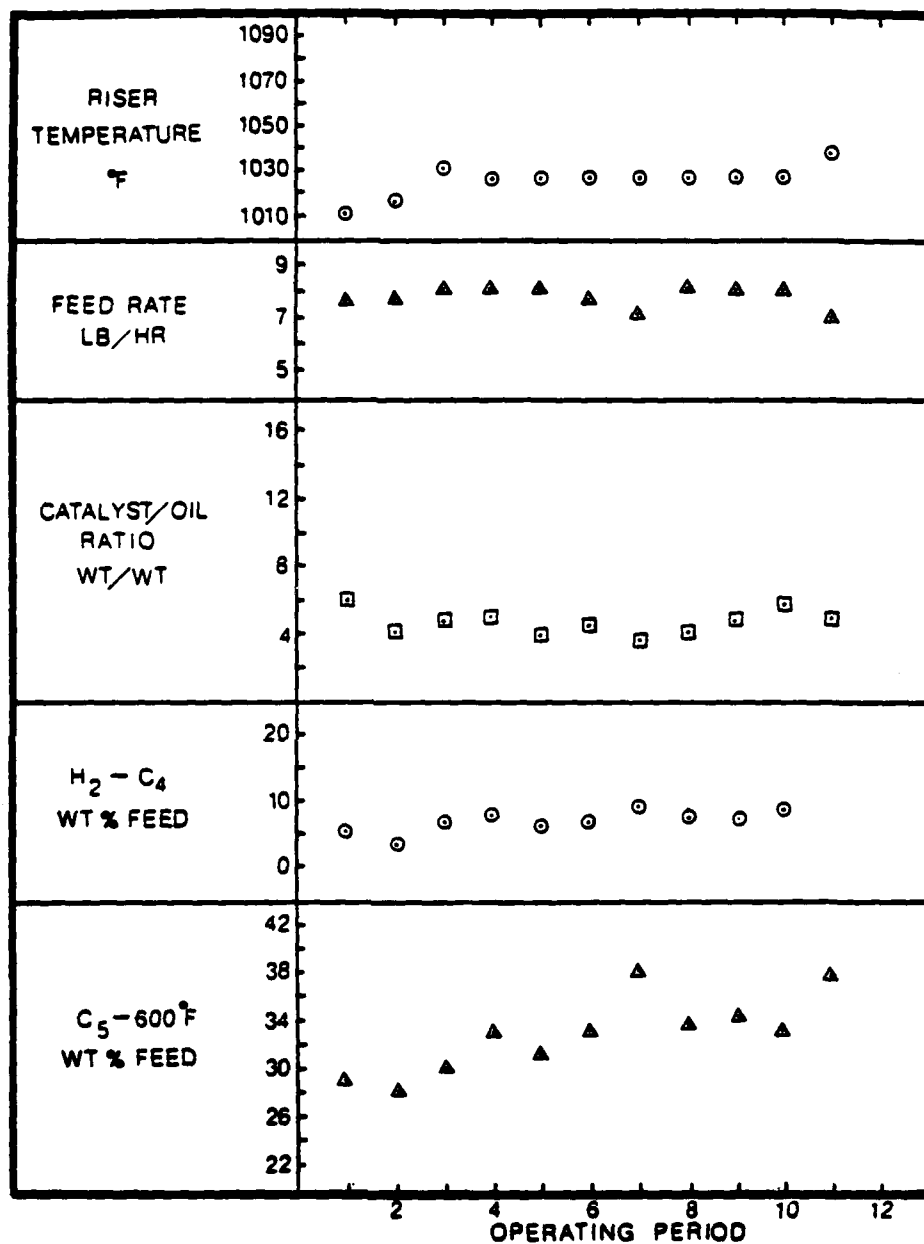


Figure 10. MRCC Run-3 Operating Conditions And Results

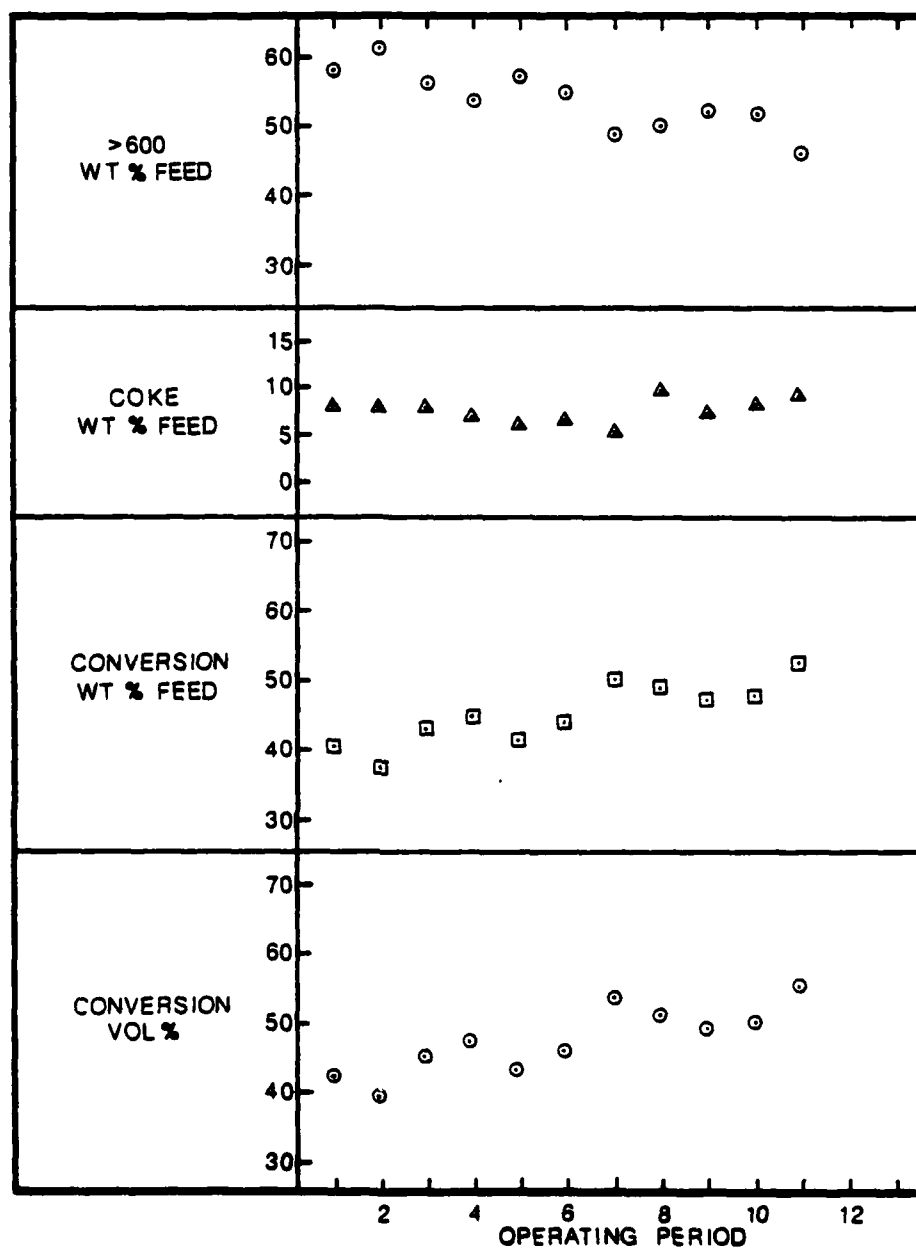


Figure 10 (Cont'd). MRCC Run-3 Operating Conditions And Results

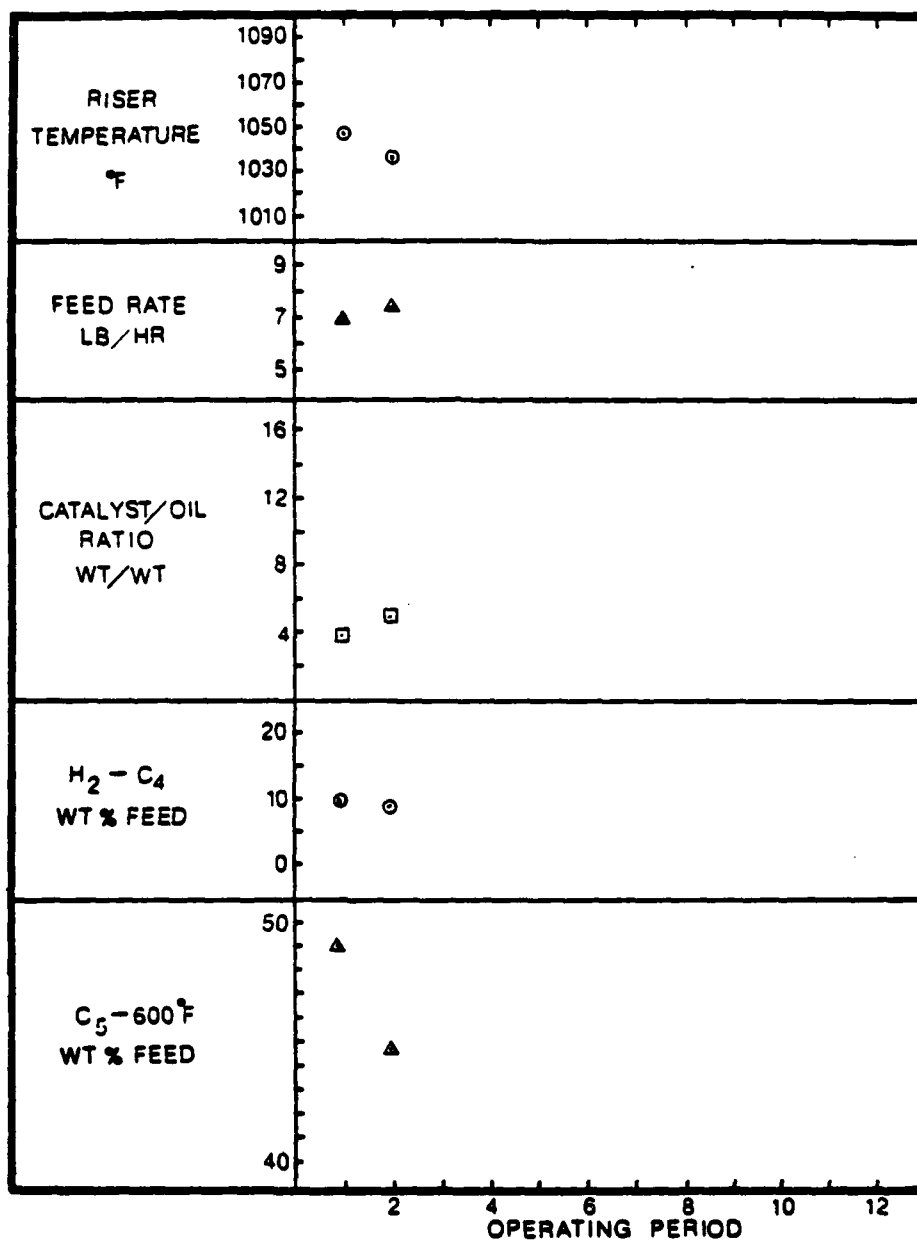


Figure 11. MRCC Run-4 Operating Conditions And Results

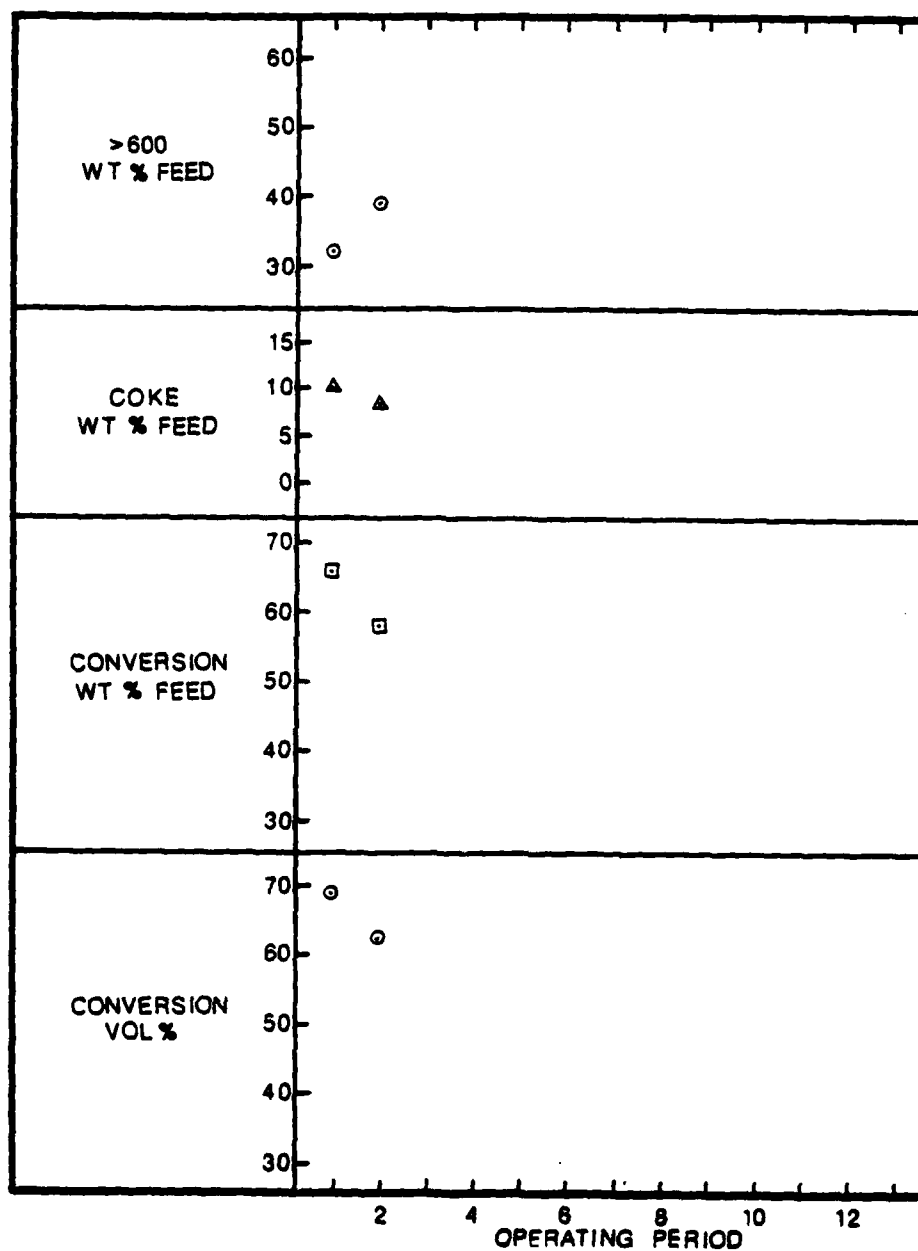


Figure 11 (Cont'd). MRCC Run-4 Operating Conditions And Results

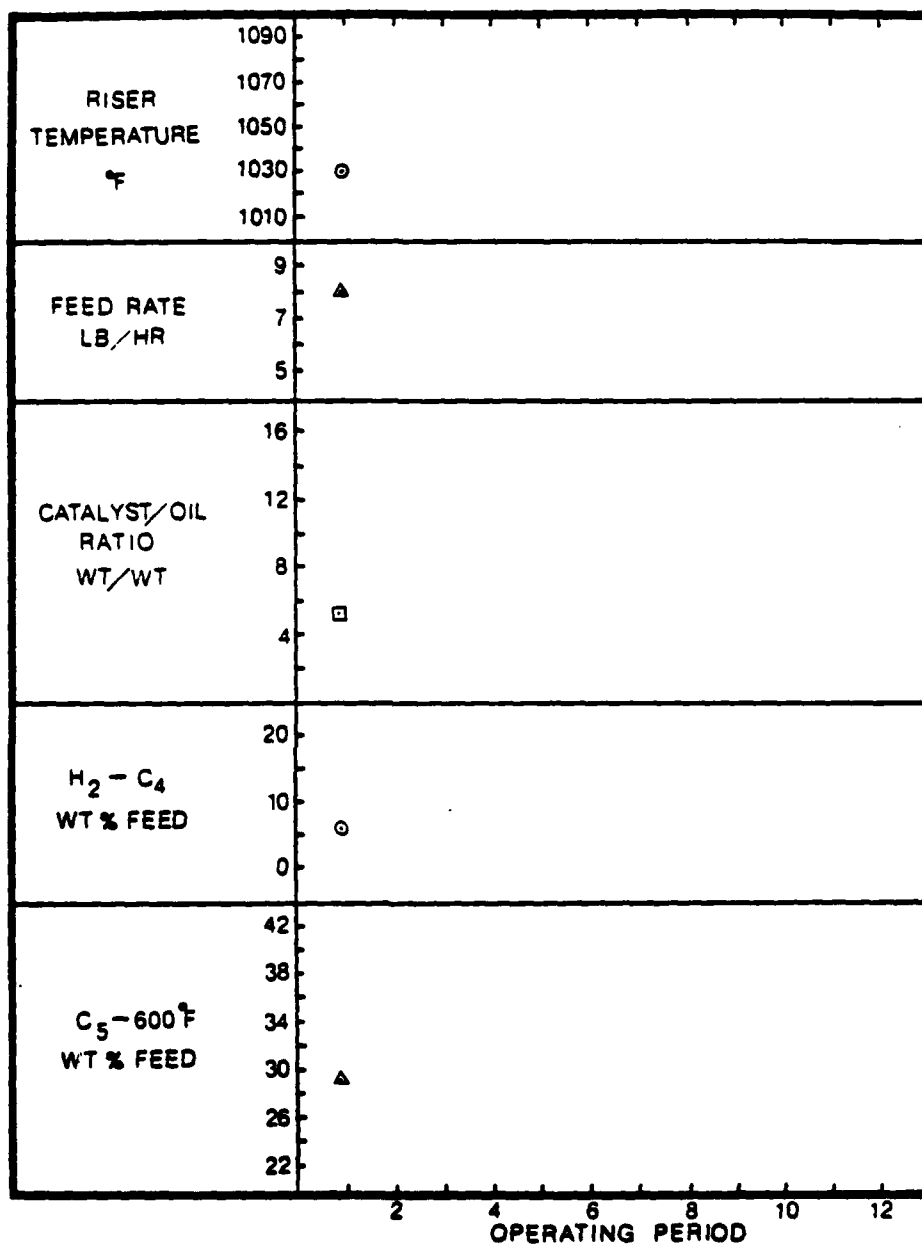


Figure 12. MRCC Run-5 Operating Conditions And Results

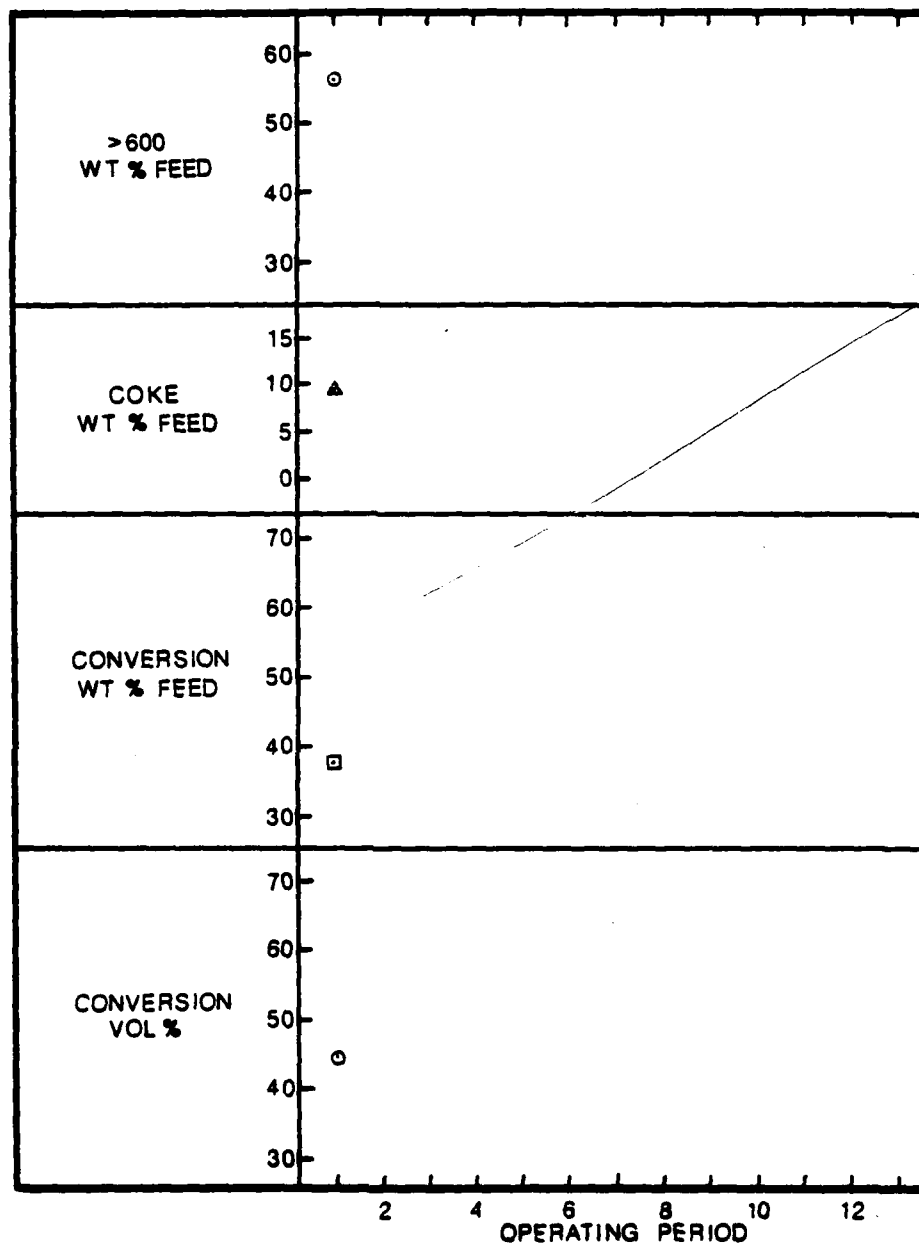


Figure 12 (Cont'd). MRCC Run-5 Operating Conditions And Results

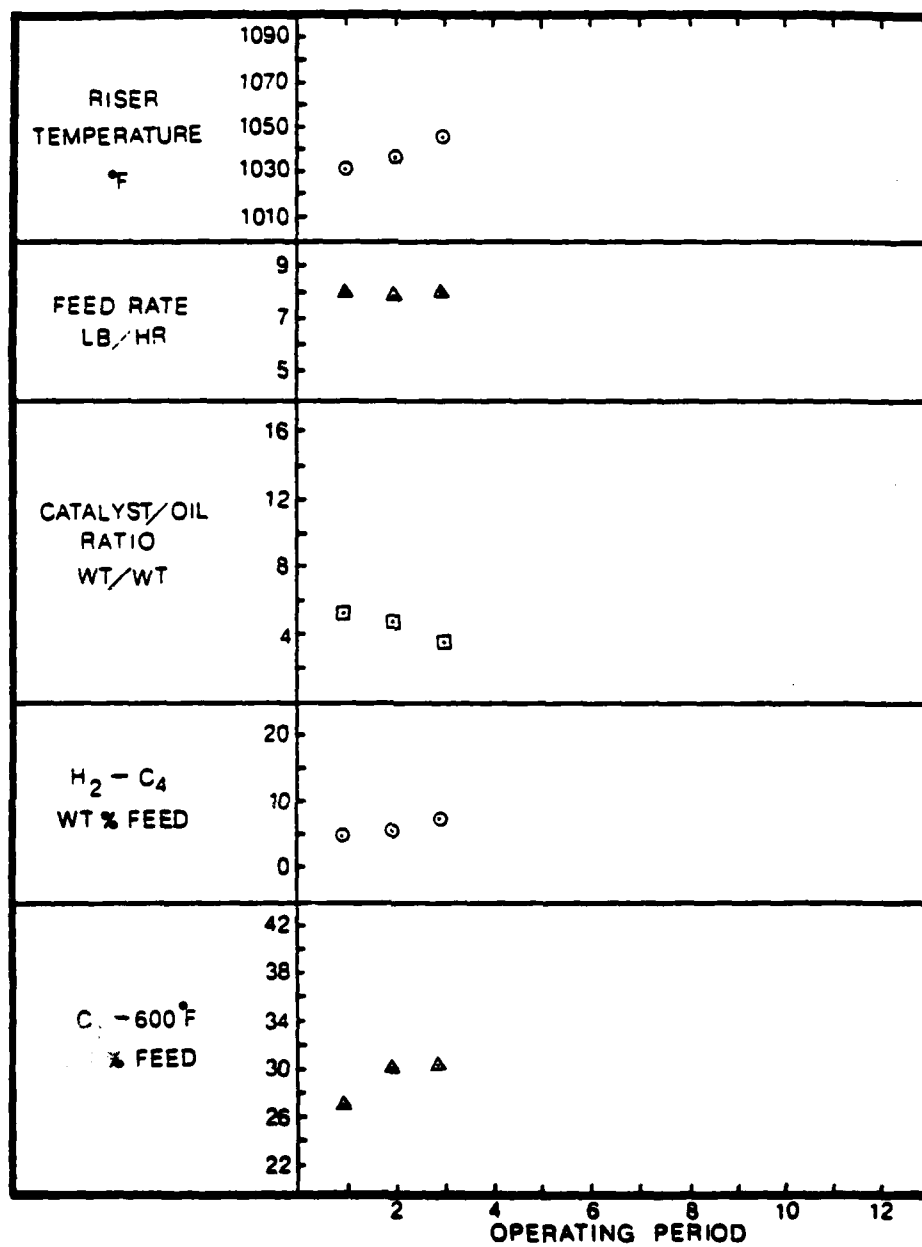


Figure 13. MRCC Run-6 Operating Conditions And Results

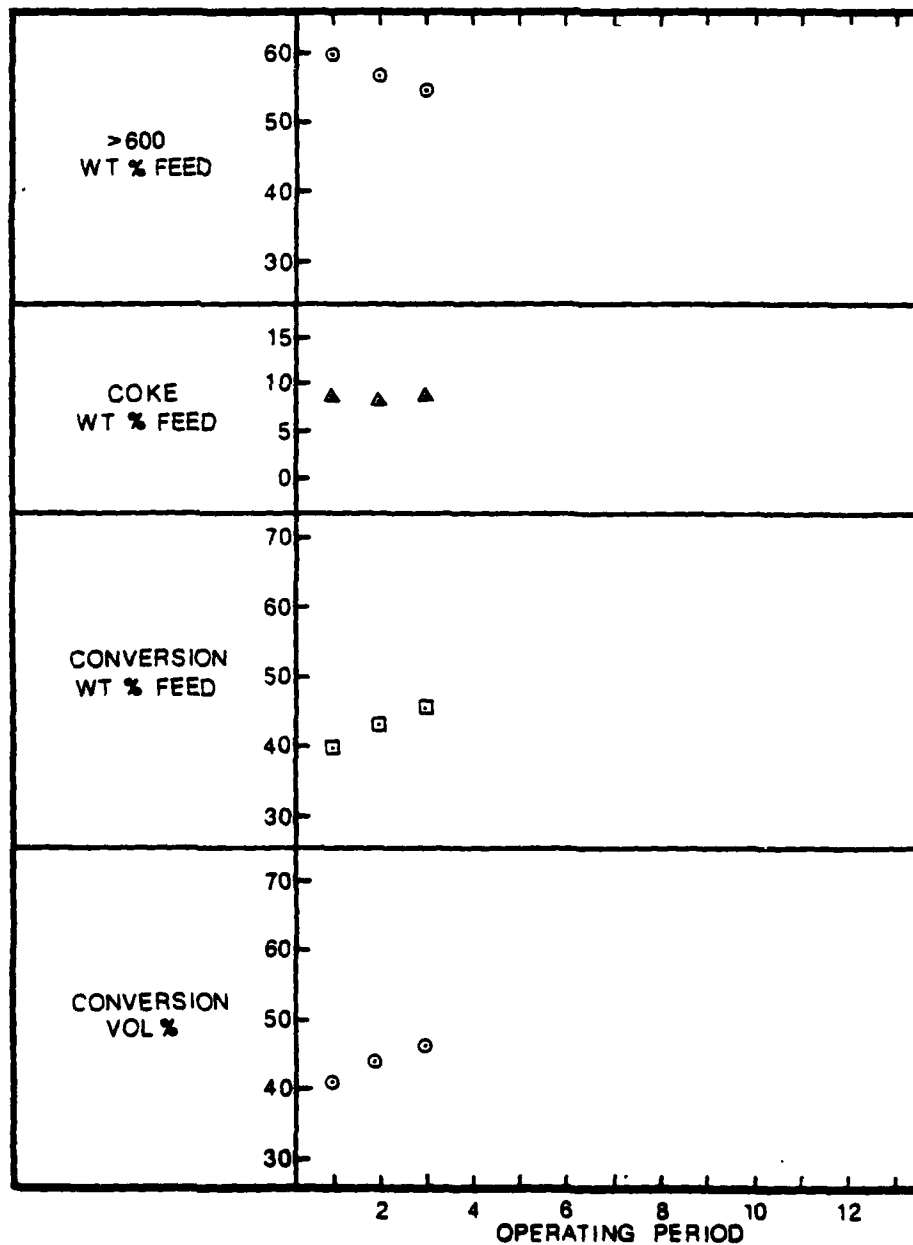


Figure 13 (Cont'd). MRCC Run-6 Operating Conditions And Results

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REFINING OF MILITARY JET FUELS FROM SHALE OIL PART III
PILOT PLANT SAMPLE PREPARATION(U) ASHLAND PETROLEUM CO
KY F H TURRILL JUL 82 AFWAL-TR-81-2056-PT-3

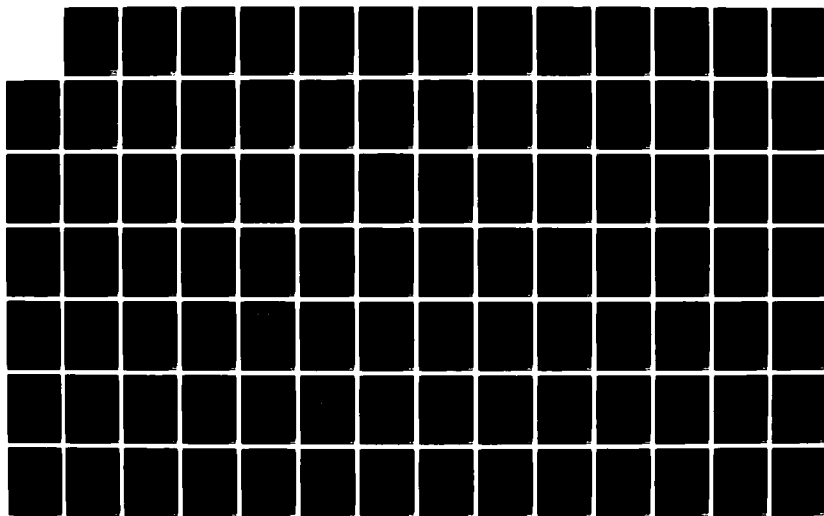
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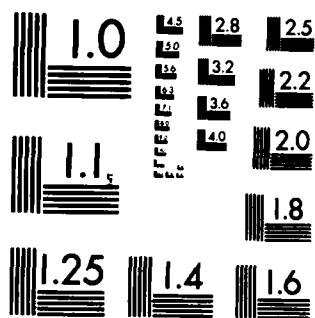
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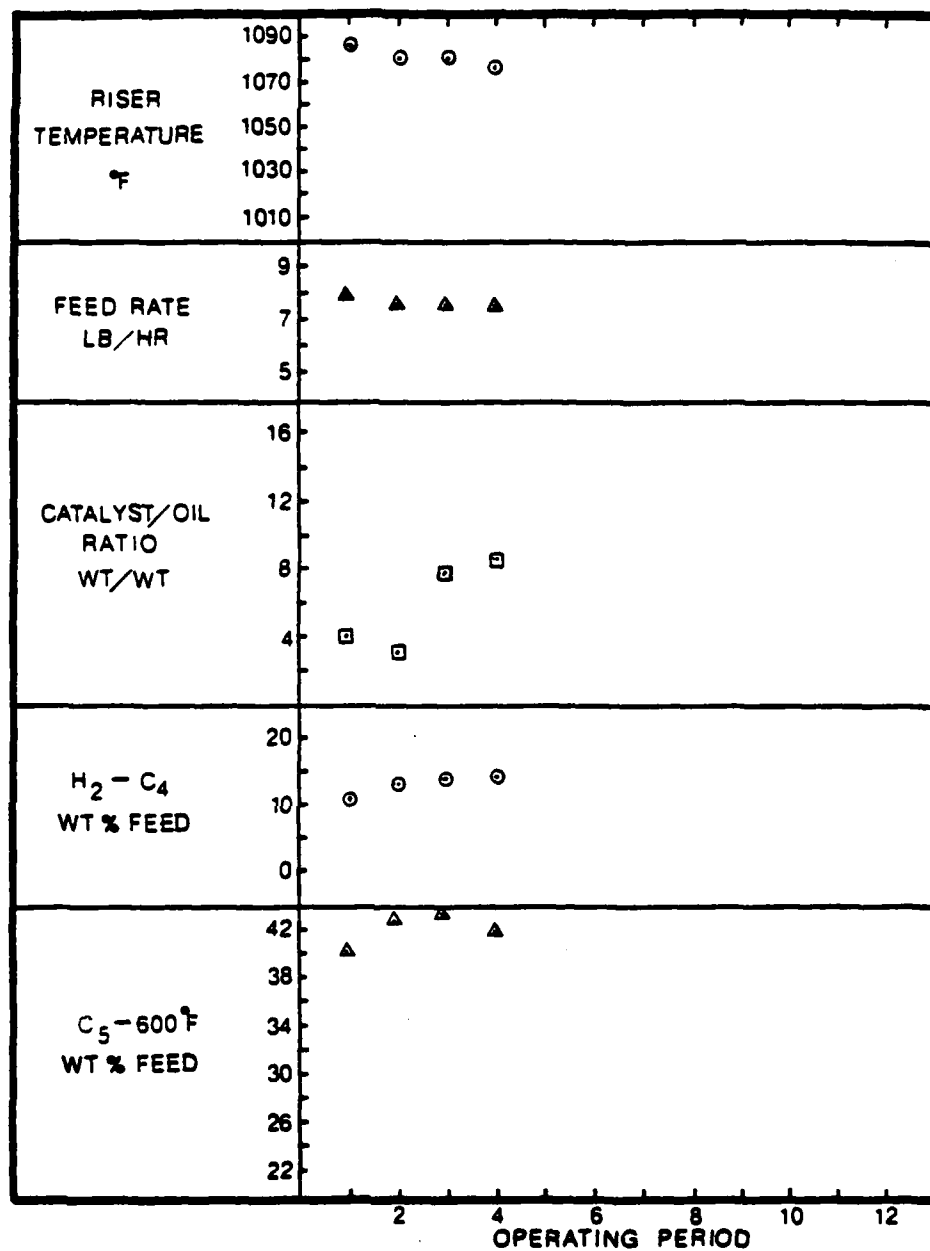


Figure 14. MRCC Run-7 Operating Conditions And Results

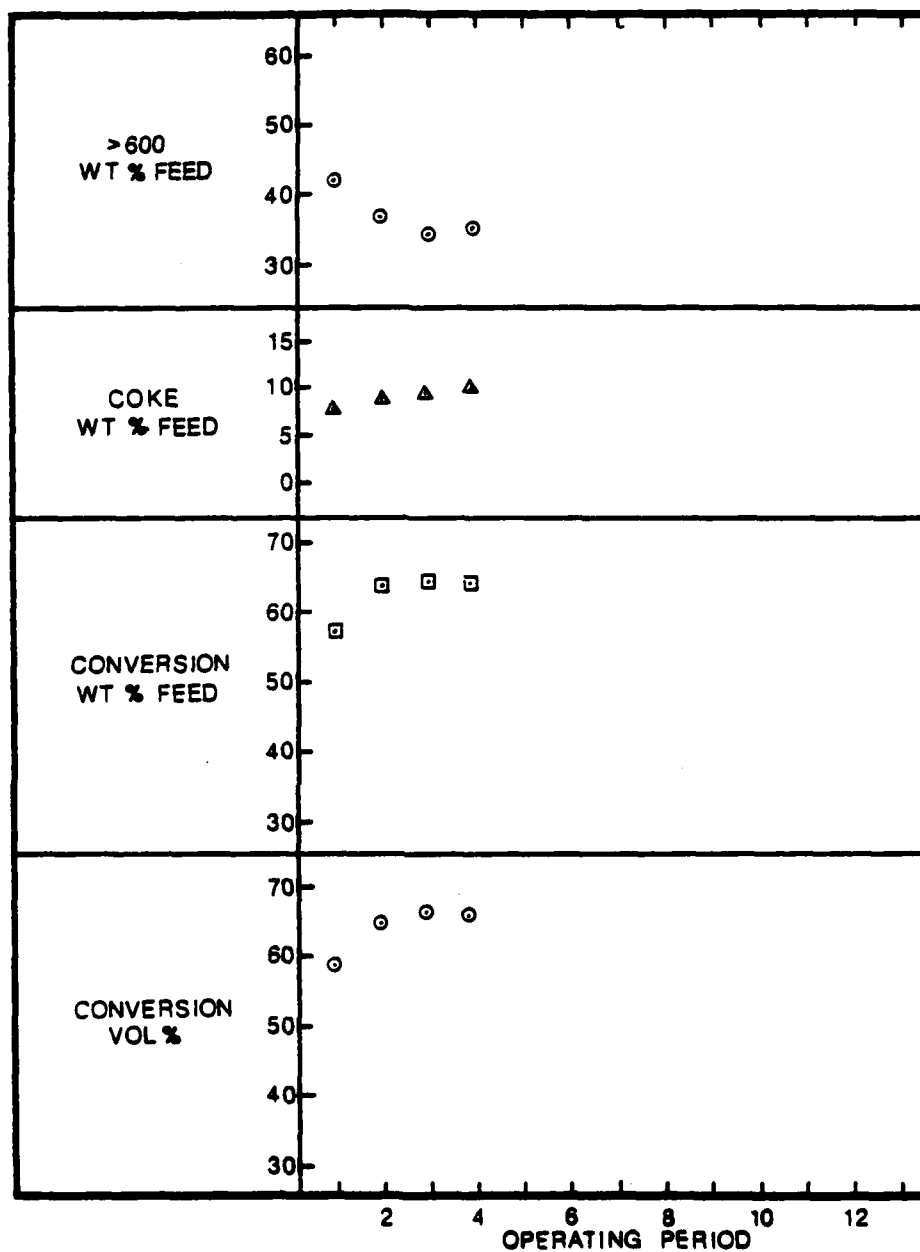


Figure 14 (Cont'd). MRCC Run-7 Operating Conditions And Results

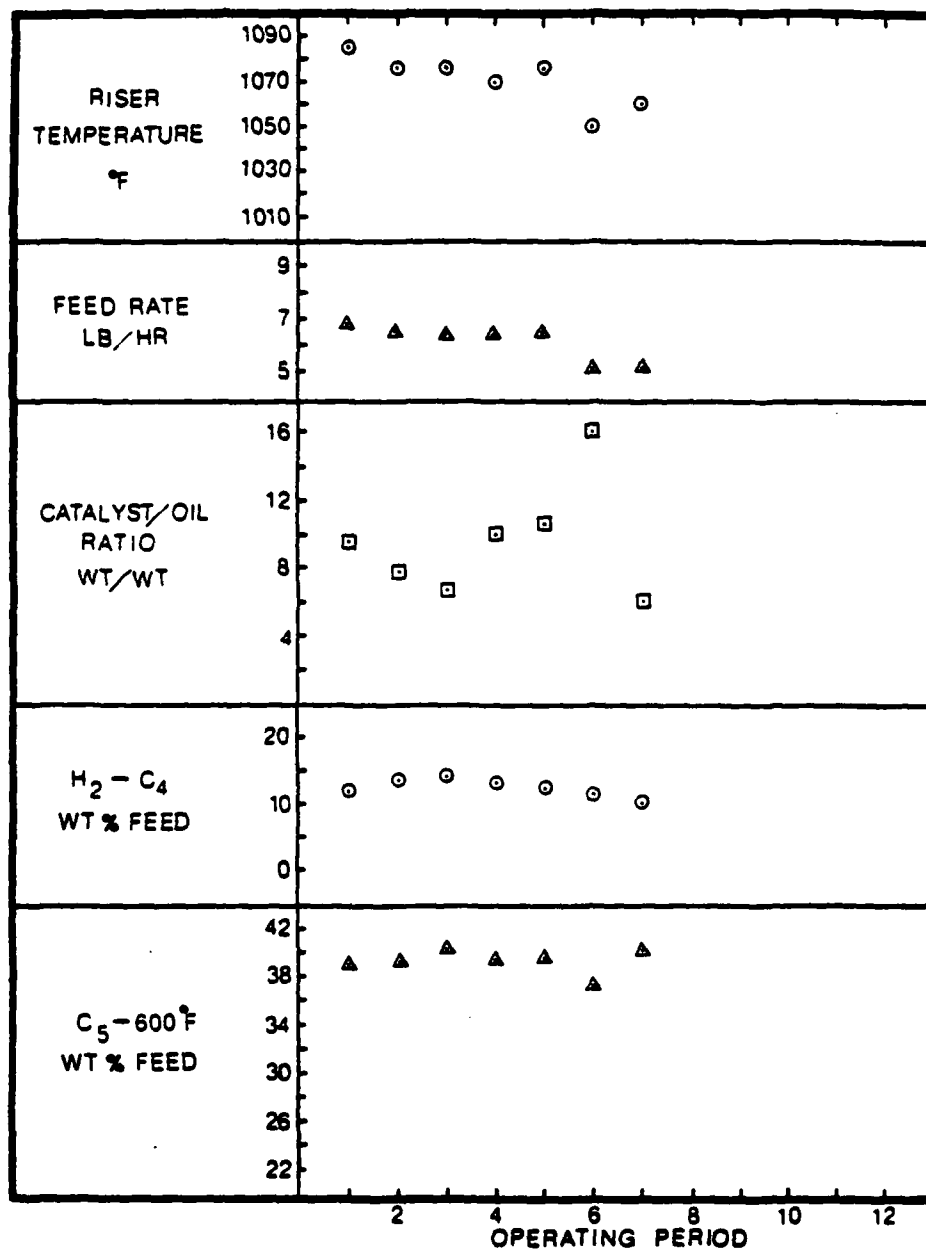


Figure 15. MRCC Run-8 Operating Conditions And Results

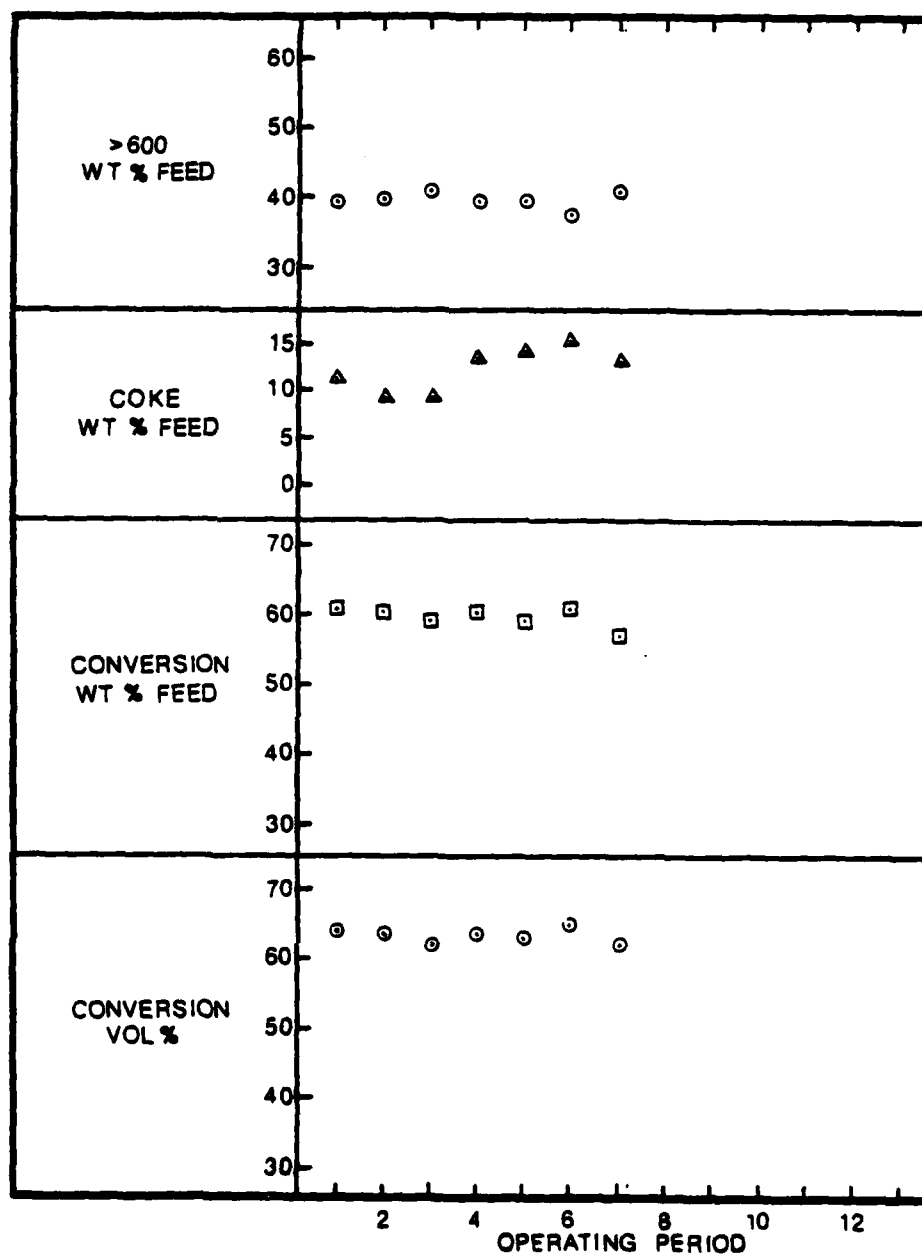


Figure 15 (Cont'd). MRCC Run-8 Operating Conditions And Results

The liquid reaction product was filtered through a five micron filter to remove catalyst fines, and composite samples from this operation were analyzed as shown by the results in Table 17.

The filtered products were fractionated using the unit shown in Figure 3 in reduced pressure mode to provide a split at close to 600°F. Analysis of component samples of the overhead, used as feedstocks in subsequent extraction operations, are given in Table 18. Composite sample analysis of the fractionator bottoms, used as feedstocks in MRCC experiments and as a residual fuel sample, are given in Table 19.

The information shown in Tables 20 through 28 was obtained by processing all data available for a given MRCC run through the material balance program, and are not simple arithmetic averages, but computer derived results which represent the overall run. The liquid properties cited are average values of the composite data given in Tables 15 and 16. Fraction data are provided where properties could be related to specific MRCC runs. MRCC run 8b was carried out to test the interplay between temperature and the catalyst/oil ratio.

A material accounting summary for this operation will be found in Section XI, Table 60.

(Continued on page 93)

TABLE 17
MRCC FULL RANGE LIQUID COMPOSITE PROPERTIES

MRCC RUN NO.	1	1	1	2	2	2	2	2	2	2	2	3	3	3	3	3	3
COMPOSITE NO.	1	2	3	3	1	2	2	2	2	2	2	1	1	2	2	2	4
API	27.3	26.7	28.2	28.4	28.9	28.2	27.7	27.8	28.4	28.4	28.4	27.7	27.8	28.4	28.4	28.4	28.4
SULFUR, WT %	0.06	0.06	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.07
NITROGEN, WT %	1.34	1.40	1.19	0.76	0.83	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.48	0.65
BASIC NITROGEN, WT %	0.44	0.53	0.42	0.31	0.34	0.33	0.36	0.31	0.29	0.28	0.28	0.36	0.31	0.29	0.29	0.28	0.28
HYDROGEN, WT %	12.1	11.8	12.3	12.4	12.4	12.2	12.0	11.9	11.9	11.7	11.7	12.0	11.9	11.9	11.9	11.9	11.7
OXYGEN, WT %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IRON, PPM	2	4	2	1	2	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	2
NICKEL, PPM	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
VANADIUM, PPM	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1
ARSENIC, PPM	-	-	-	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
RAMSBOTTOM CARBON, WT %	0.54	0.49	0.39	0.39	0.35	0.26	0.38	0.48	0.48	0.48	0.48	0.38	0.48	0.48	0.48	0.48	0.48
DISTILLATION, 02887(WT% ¹ F)																	
IBP.	-	133	146	157	159	167	99	132	110	135	135	99	132	110	135	135	135
5	-	274	251	255	273	281	230	255	224	227	227	230	255	224	227	227	227
10	-	342	318	333	344	346	286	328	281	284	284	286	328	281	284	284	284
50	-	644	670	658	663	644	639	643	644	642	642	639	643	644	642	642	642
90	-	874	856	846	835	842	820	836	825	824	824	820	836	825	824	824	824
95	-	924	911	888	869	867	868	874	871	870	870	868	874	871	870	870	870
EP	-	1016	1004	970	927	970	922	928	943	943	943	922	928	943	943	943	943
GROSS HEATING VALUE, BTU/LB	19087	19,055	19,123	19,133	19,152	19,127	19,081	19,038	19,030	19,054	19,054	19,081	19,038	19,030	19,054	19,054	19,054
AVERAGE WT % FEED	(78.3)	(78.3)	(78.3)	(79.1)	(79.1)	(79.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)	(77.1)

TABLE 17 (CONT'D)

MRCC FULL RANGE LIQUID COMPOSITE PROPERTIES

MRCC RUN NO.	4	5	6	7	7	8	8	8
COMPOSITE NO.	1	1	1	1	2	1	2	3
API	31.9	26.9	26.6	28.6	28.7	23.3	22.8	22.2
SULFUR, WT %	0.01	0.07	0.05	0.07	0.07	0.08	0.07	0.07
NITROGEN, WT %	0.28	1.21	0.47	0.99	1.0	0.48	0.53	0.58
BASIC NITROGEN, WT %	0.10	0.59	0.12	0.47	0.40	0.19	0.16	0.20
HYDROGEN, WT %	12.0	10.1	11.6	11.7	11.7	9.8	10.6	10.8
OXYGEN, WT %	-	-	-	-	-	-	-	-
IRON, PPM	<1	1	1	2	1	<1	1	1
NICKEL, PPM	<1	<1	<1	<1	<1	<1	<1	<1
VANADIUM, PPM	1	<1	<1	1	<1	<1	<1	<1
ARSENIC, PPM	<1	<1	<1	-	-	<1	<1	<1
RAMSBOTTOM CARBON, WT %	0.59	0.30	0.66	0.86	0.84	1.37	1.7	1.6
DISTILLATION, D2887(WT %N°F)								
IBP.	78	175	116	87	94	96	107	112
5	168	286	228	181	203	191	211	235
10	219	369	289	239	251	237	286	288
50	610	660	656	606	601	626	623	633
90	800	841	815	826	817	777	775	803
95	852	879	858	882	866	821	821	861
EP	931	933	939	983	943	889	892	982
GROSS HEATING VALUE, BTU/LB	19,168	19,125	18,982	19,068	18,964	18,725	18,640	18,684
AVERAGE WT % FEED	(69.5)	(71.0)	(78.5)	(69.0)	(69.0)	(67.4)	(67.4)	(67.4)

TABLE 18

MRCC OVERHEAD COMPOSITES (<600°F)

MRCC RUN NO.	1	1	1	2	3	4	5	6	7	8
COMPOSITE NO.	1	2	3	4	5	6	7	8	9	10
API	38.5	37.3	35.9	36.6	37.7	37.6	36.1			
SULFUR, WT %	0.04	0.03	0.03	0.04	0.04	0.04	0.04	0.04		
NITROGEN, WT %	0.99	1.00	0.66	0.58	0.65	0.76	0.32			
BASIC NITROGEN, WT %	0.52	0.51	0.40	0.44	0.27	0.37	0.14			
HYDROGEN, WT %	12.0	12.2	12.1	11.9	12.0	9.8	11.3			
OXYGEN, WT %	-	-	-	-	-	-	-			
IRON, PPM	3	1	1	<1	1	2	<1			
NICKEL, PPM	<1	<1	<1	<1	<1	<1	<1			
VANADIUM, PPM	<1	<1	<1	<1	1	<1	<1			
ARSENIC, PPM	<1	<1	<1	<1	<1	<1	<1			
RAMSBOTTOM CARBON, WT %	0.24	0.18	0.10	0.19	0.18	0.32	0.34			
DISTILLATION, D2887 (WT % X °F)										
IBP	139	116	51	166	135	131	127			
5	187	185	208	211	201	192	191			
10	213	221	247	248	232	221	222			
50	387	409	448	418	394	374	365			
90	533	574	600	585	577	551	541			
95	559	597	606	598	598	578	571			
EP	799	621	627	612	622	612	615			
GROSS HEATING VALUE, BTU/LB	19,068	19,119	-	18,954	19,158	19,118	18,939			
AVERAGE WT % FEED	(19.4)	(19.4)	(23.2)	(24.9)	(21.7)	(27.4)	(22.9)			

TABLE 19

MRC RUN NO.	1	1	2	2	3	3	3	3	3
COMPOSITE NO.	1	2	1	2	1	1	1	2	1
%API	23.5	23.5	26.4	24.3	23.6	22.1	21.3	21.3	13.6
SULFUR, WT %	0.06	0.05	0.04	0.04	0.06	0.07	0.07	0.06	0.09
NITROGEN, WT %	1.08	0.96	0.57	0.58	0.54	0.71	0.62	0.78	0.64
BASIC NITROGEN, WT %	0.47	0.48	0.31	0.31	0.36	0.27	0.21	0.30	0.14
HYDROGEN, WT %	11.9	12.1	12.2	12.1	-	11.7	11.6	11.4	10.2
OXYGEN, WT %	-	-	-	-	-	-	-	-	-
IRON, PPM	4	8	6	<1	1	3	4	4	2
NICKEL, PPM	<1	1	1	<1	<1	<1	<1	<1	<1
VANADIUM, PPM	<1	1	1	<1	<1	1	1	1	1
ARSENIC, PPM	1	<1	<1	<1	<1	<1	<1	<1	<1
RAMSBOTTOM CARBON, WT %	0.73	0.65	0.49	0.35	0.40	0.85	0.68	1.16	2.9
DISTILLATION, D2887(WT%N°F)									
IBP.	554	539	569	605	592	583	557	530	217
5	603	620	615	622	615	612	614	596	466
10	619	631	626	643	627	627	627	609	597
50	732	734	722	731	714	712	707	701	676
90	887	877	870	880	858	868	855	869	808
95	928	909	913	922	892	919	893	917	844
EP	978	944	978	988	943	1,014	947	1,001	896
GROSS HEATING VALUE, BTU/LB	19,014	19,059	19,162	19,162	19,036	19,000	18,887	19,108	18,341
AVERAGE WT % FEED	(55.8)	(55.8)	(53.0)	(53.0)	(65.1)	(51.2)	~(51.2)	(37.8)	(40.8)

TABLE 20
MODIFIED REDUCED CRUDE
CONVERSION RUN-1

FEEDSTOCK : 100 % CSHT

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1020	°API	24.2	27.4	37.9	23.5
Cat/Oil Ratio	4.4	Carbon, %_w	-	-	-	-
C on Regen Cat, %	0.11	Hydrogen, %_w	12.2	12.1	12.1	12.0
Conversion, Wt %^a	43.36	Nitrogen, %_w	1.28	1.06	1.00	1.02
Closure, Wt %	100.03	N_{basic}, %_w	0.74	0.46	0.52	0.48
		Sulfur, %_w	0.10	0.05	0.04	0.06
		Oxygen, %_w	-	-	-	-
		Rams C, %_w	0.91	0.47	0.21	0.69
		Aromatics, %_w	-	-	-	-
		GHV, Btu/lb	19,082	19,088	19,094	19,036
		Distillation, Wt % (°F) by				
		IBP	596	150	128	577
		5	618	263	186	612
		10	633	330	217	625
		50	760	677	398	733
		90	909	866	554	882
		95	938	918	578	919
		BP	959	1010	624	962
Product Yields, Wt %						
H₂	0.17					
C₁	0.71					
C₂	1.40					
C₃	0.50					
C₃^m	1.66					
iC₄	0.27					
nC₄	0.21					
C₄^m	2.14					
C₅ - 600	28.83					
600 +	56.08					
Coke	8.02					

a - Based on the specified cut point above

TABLE 21
MODIFIED REDUCED CRUDE
CONVERSION RUN-2

FEEDSTOCK : 80 % CSHT , 40 % COHT

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1020	°API	24.7	28.8	35.9	24.4
Cat/Oil Ratio	4.0	Carbon, % _w	-	-	-	-
C on Regen Cat, %	0.16	Hydrogen, % _w	-	12.3	12.1	12.2
Conversion, Wt %^a	41.62	Nitrogen, % _w	0.94	0.70	0.66	0.58
Closure, Wt %	99.14	Nbasic, % _w	0.56	0.33	0.40	0.31
		Sulfur, % _w	0.06	0.04	0.03	0.04
		Oxygen, % _w	-	-	-	-
		Rams C, % _w	0.50	0.33	0.10	0.42
		Aromatics, % _w	-	-	-	-
		GHV, Btu/lb	19,164	19,138	-	19,162
		Distillation, Wt % (°F) by				
		IBP	525	161	51	587
		5	602	270	208	619
		10	617	348	247	630
		50	743	662	448	727
		90	903	841	600	875
		95	939	881	606	918
		EP	984	956	627	983
Product Yields, Wt %						
H ₂	0.16					
C ₁	0.63					
C ₂	1.20					
C ₃	0.44					
C ₃ ^m	1.58					
iC ₄	0.25					
nC ₄	0.20					
C ₄ ^m	1.92					
C ₅ - 600	29.64					
600+	56.23					
Coke	7.75					

^a - Based on the specified cut point above

TABLE 22

MODIFIED REDUCED CRUDE CONVERSION RUN-3

FEEDSTOCK : 80 % CSHT , 40 % MRCC RECYCLE

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1025	°API	24.1	28.1	36.6	23.6
Cat/Oil Ratio	4.4	Carbon, % _w	-	-	-	-
C on Regen Cat, %	0.27	Hydrogen, % _w	-	11.9	11.9	-
Conversion, Wt % ^a	45.37	Nitrogen, % _w	0.80	0.59	0.58	0.54
Closure, Wt %	97.87	N _{basic} , % _w	0.58	0.31	0.44	0.36
		Sulfur, % _w	0.07	0.06	0.04	0.06
		Oxygen, % _w	-	-	-	-
		Rams C, % _w	0.59	0.51	0.19	0.60
		Aromatics, % _w	-	-	-	-
		GHV, Btu/lb	19,144	19,051	18,954	19,036
		Distillation, Wt % (°F) by				
		IBP	535	119	146	599
		5	606	234	211	615
		10	624	295	248	627
		50	734	647	418	714
		90	892	828	585	858
		95	936	871	598	892
		EP	971	943	612	943
Product Yields, Wt %		H ₂	0.19			
		C ₁	0.84			
		C ₂	1.47			
		C ₃	0.50			
		C ₃ ⁼	1.90			
		iC ₄	0.28			
		nC ₄	0.21			
		C ₄ ⁼	2.25			
		C ₅ - 600	32.09			
		600 +	53.00			
		Coke	7.25			

- a - Based on the specified cut point above

TABLE 23

MODIFIED REDUCED CRUDE CONVERSION RUN-4

FEEDSTOCK 100 % COHT

Operating Conditions		Liquid Properties			
		Item	Feed	Total Product	- 600°F + 600°F
Temperature, °F	1040	°API	26.1	31.9	
Cat/Oil Ratio	4.0	Carbon, % _w	-	-	
C on Regen Cat, %	0.11	Hydrogen, % _w	12.7	12.0	
Conversion, Wt % ^a	61.6	Nitrogen, % _w	0.61	0.28	
Closure, Wt %	95.18	N _{basic} , % _w	0.32	0.10	
		Sulfur, % _w	0.01	0.01	
		Oxygen, % _w	-	-	
		Rams C, % _w	0.64	0.59	
		Aromatics, % _w	-	-	
		GHV, Btu/lb	19,288	19,168	
		Distillation, Wt % (°F) by			
		IBP	390	78	
		5	575	168	
		10	606	219	
		50	715	610	
		90	873	800	
		95	910	852	
		EP	947	931	
Product Yields, Wt %					
		H ₂	0.13		
		C ₁	0.61		
		C ₂	1.08		
		C ₃	0.90		
		C ₃ ⁼	2.80		
		iC ₄	0.87		
		nC ₄	0.23		
		C ₄ ⁼	4.21		
		C ₅ - 600	45.16		
		600+	35.27		
		Coke	8.75		

^a - Based on the specified cut point above

TABLE 24

MODIFIED REDUCED CRUDE CONVERSION RUN-5

FEEDSTOCK : 95 % CSHT , 5 % ACID EXTRACT

Operating Conditions		Liquid Properties			
		Item	Feed	Total Product	- 600°F + 600°F
Temperature, °F	1035	°API	23.1	26.9	
Cat/Oil Ratio	5.0	Carbon, % _w	-	-	
C on Regen Cat, %	0.10	Hydrogen, % _w	-	10.1	
Conversion, Wt % ^a	37.78	Nitrogen, % _w	1.42	1.21	
Closure, Wt %	92.12	N _{basic} , % _w	1.10	0.59	
		Sulfur, % _w	0.09	0.07	
		Oxygen, % _w	-	-	
		Rams C, % _w	0.70	0.30	
		Aromatics, % _w	-	-	
		GHV, Btu/lb	-	19,125	
		Distillation, Wt % (°F) by			
		IBP	406	175	
		5	556	286	
		10	604	369	
		50	735	660	
		90	914	841	
		95	947	879	
		BP	992	933	
Product Yields, Wt %					
H ₂	0.09				
C ₁	0.70				
C ₂	1.37				
C ₃	0.40				
C ₃ ^m	1.43				
iC ₄	0.11				
nC ₄	0.14				
C ₄ ^m	1.51				
C ₅ - 600	28.72				
600+	56.00				
Coke	9.53				

- a - Based on the specified cut point above

FEEDSTOCK : 100 % MRCC RECYCLE

a - Based on the specified cut point above

TABLE 26
MODIFIED REDUCED CRUDE
CONVERSION RUN-7

FEEDSTOCK : 100 % CSHT

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1080	°API	24.0	28.7		
Cat/Oil Ratio	5.9	Carbon, % _w	-	-		
C on Regen Cat, %	0.13	Hydrogen, % _w	-	11.7		
Conversion, Wt % ^a	62.33	Nitrogen, % _w	1.46	1.00		
Closure, Wt %	62.33	N _{basic} , % _w	0.80	0.44		
		Sulfur, % _w	0.11	0.07		
		Oxygen, % _w	-	-		
		Rams C, % _w	0.65	0.85		
		Aromatics, % _w	-	-		
		GHV, Btu/lb	19,023	19,016		
		Distillation, Wt % (°F) by				
		IBP	582	91		
		5	601	192		
		10	617	245		
		30	756	604		
		90	920	822		
		95	948	874		
		EP	1000	963		
Product Yields, Wt %						
		H ₂	0.24			
		C ₁	1.77			
		C ₂	3.36			
		C ₃	0.82			
		C ₃ ⁼	3.53			
		iC ₄	0.27			
		nC ₄	0.29			
		C ₄ ⁼	3.56			
		C ₅ - 600	40.79			
		600+	36.47			
		Coke	8.89			

a - Based on the specified cut point above

TABLE 27

MODIFIED REDUCED CRUDE CONVERSION RUN-8A

FEEDSTOCK : 100 % MRCC RECYCLE

Operating Conditions	Liquid Properties				
	Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F 1075	°API	21.7	23.1		
Cat/Oil Ratio 8.8	Carbon, % _w	-	-		
C on Regen Cat, % 0.10	Hydrogen, % _w	11.7	10.2		
Conversion, Wt % ^a 59.59	Nitrogen, % _w	0.66	0.51		
Closure, Wt % 101.73	Nbasic, % _w	0.24	0.18		
	Sulfur, % _w	0.07	0.08		
	Oxygen, % _w	-	-		
	Rams C, % _w	0.81	0.18		
	Aromatics, % _w	-	-		
	GHV, Btu/lb	18,944	18,683		
	Distillation, Wt % (°F) by				
	IBP	520	102		
	5	613	201		
	10	627	262		
	50	710	625		
	90	862	776		
	95	906	821		
	EP	981	891		
Product Yields, Wt %					
H ₂ 0.20					
C ₁ 1.77					
C ₂ 2.71					
C ₃ 0.77					
C ₃ ^m 3.89					
iC ₄ 0.85					
nC ₄ 0.33					
C ₄ ^m 4.28					
C ₅ - 600 34.92					
600+ 39.40					
Coke 10.86					

- a - Based on the specified cut point above

TABLE 28
MODIFIED REDUCED CRUDE
CONVERSION RUN-8B

FEEDSTOCK : 100 % MRCC RECYCLE

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F 1050		°API	21.5	22.2		
Cat/Oil Ratio 14.3		Carbon, % _w	-	-		
C on Regen Cat, % 0.05		Hydrogen, % _w	11.4	10.8		
Conversion, Wt % ^a 59.58		Nitrogen, % _w	0.78	0.58		
Closure, Wt % 102.8		N _{basic} , % _w	0.30	0.20		
		Sulfur, % _w	0.06	0.07		
		Oxygen, % _w	-	-		
		Rams C, % _w	0.68	1.60		
		Aromatics, % _w				
		GHV, Btu/lb	19,108	18,684		
		Distillation, Wt % (°F) by				
		IBP	430	112		
		5	596	235		
		10	609	288		
		50	701	633		
		90	869	803		
		95	917	861		
		EP	1001	982		
Product Yields, Wt %						
H ₂	0.23					
C ₁	1.75					
C ₂	2.57					
C ₃	0.6					
C ₃ ^m	3.2					
iC ₄	0.44					
nC ₄	0.19					
C ₄ ^m	3.64					
C ₅ - 600	35.16					
600.+	37.94					
Coke	14.27					

^a - Based on the specified cut point above

5. DISCUSSION

Both conversion and distillate yields are lower than those which would be expected from a "normal" petroleum feedstock of comparable gravity and distillation range. Undoubtedly, an important factor contributing to this difference is the high basic nitrogen level in shale derived MRCC feedstocks.

Phase III MRCC conversion and distillate yields were also lower than those obtained during Phase II runs using the same reactor system. These differences between the Phase II and Phase III results may be due to several factors:

- A. Significantly higher catalyst-to-oil ratios were used in Phase II.
- B. Much shorter run times were used in Phase II because of the limited quantities of feedstock available.
- C. Compositional differences in the hydrogenated feedstock attributable to the lower hydrogenation, hydrodesulfurization, and hydrodenitrogenation activities of the partially fouled Phase III CSHT catalyst.

The combination of the short run times and high catalyst/oil ratios used in Phase II precluded achievement of steady-state operation of the catalyst as compared with the

longer Phase III MRCC runs which appear to have resulted in the lower conversions and distillate yields.

Inspection of the data presented in Tables 20 through 28 indicates that the MRCC process did accomplish non-hydrogenative reductions in both the sulfur and nitrogen contents in addition to the expected cascading of boiling range. Hydrogen redistribution to the distillate fraction by the less active, steady-state catalyst was not demonstrated in the Phase III MRCC results.

MRCC run 8 was divided into two experimental sections (A & B) in an attempt to maintain conversion level by increasing the catalyst/oil ratio while decreasing the riser temperature. The results, as shown in Tables 16, 27, and 28 indicate that the attempt was successful.

A comparison of the data shown in Tables 15, 16, 18 and 19 shows that a source of iron contamination was present in the product handling and fractionation equipment, and that iron was deposited on the catalyst. The effect of this iron deposition on conversion and other MRCC results is not known at this time.

6. CONCLUSIONS

- The MRCC unit was operated quite successfully over a period of approximately six months with a number of shale derived feedstocks, and demonstrated that shale conversion can be successfully carried out on a sustained, continuous basis.
- Good nitrogen and sulfur removal was observed with all feedstocks investigated. This non-hydrogenative heteroatom removal constitutes an economic bonus from the MRCC process.
- The lower conversions and distillate yields obtained compared to petroleum feedstocks at comparable processing conditions are ascribed to the very high basic nitrogen levels present in shale derived feedstocks. Present MRCC operations would correct this activity requirement with a new, proprietary catalyst developed by Ashland for its RCC process.
- Unhydrotreated MRCC recycle can be successfully reprocessed by admixture with fresh feed. To obtain the maximum benefits of recycle oil hydrotreating, the hydrotreated product should be reprocessed in the MRCC on a blocked out operation using hydrotreated feed only.

- The somewhat lower conversions and distillate yields obtained in Phase III, as compared to Phase II, are ascribed to differences in feedstock quality, problems related to long-term operations in a small pilot unit involving new and only partially mastered technology, and to long-term operation on an equilibrium catalyst.

SECTION V

ACID EXTRACTION

1. OBJECTIVE

The objective of acid extraction is to remove a large portion of the basic nitrogen containing compounds from both converted and straight run shale distillates without the use of external hydrogen. This operation forms the extraction portion of Ashland's EXTRACTACRACKING process.

2. MECHANICAL DESCRIPTION

Acid extraction was performed in the countercurrent extraction equipment shown in Figure 16. The York-Scheibel extraction column shown consisted of 10 actual agitated stages. Temperature near the interface of the liquid phases was maintained by use of heat tapes attached to both the column and the oil charge line. Open loop control using Variacs proved adequate to maintain the desired extraction temperature. The extract phase was stored for further recovery and evaluation. The raffinate was processed to remove traces of mineral acid as shown in Figure 17. Two procedures for raffinate purification were studied. In extractor runs 1 and 2 the raffinate was collected and washed in off-line equipment as indicated in Figure 17. Successive washes with dilute sodium hydroxide and water provided the required contaminant removal. In the case of extractor run 3, raffinate direct from the extractor was percolated

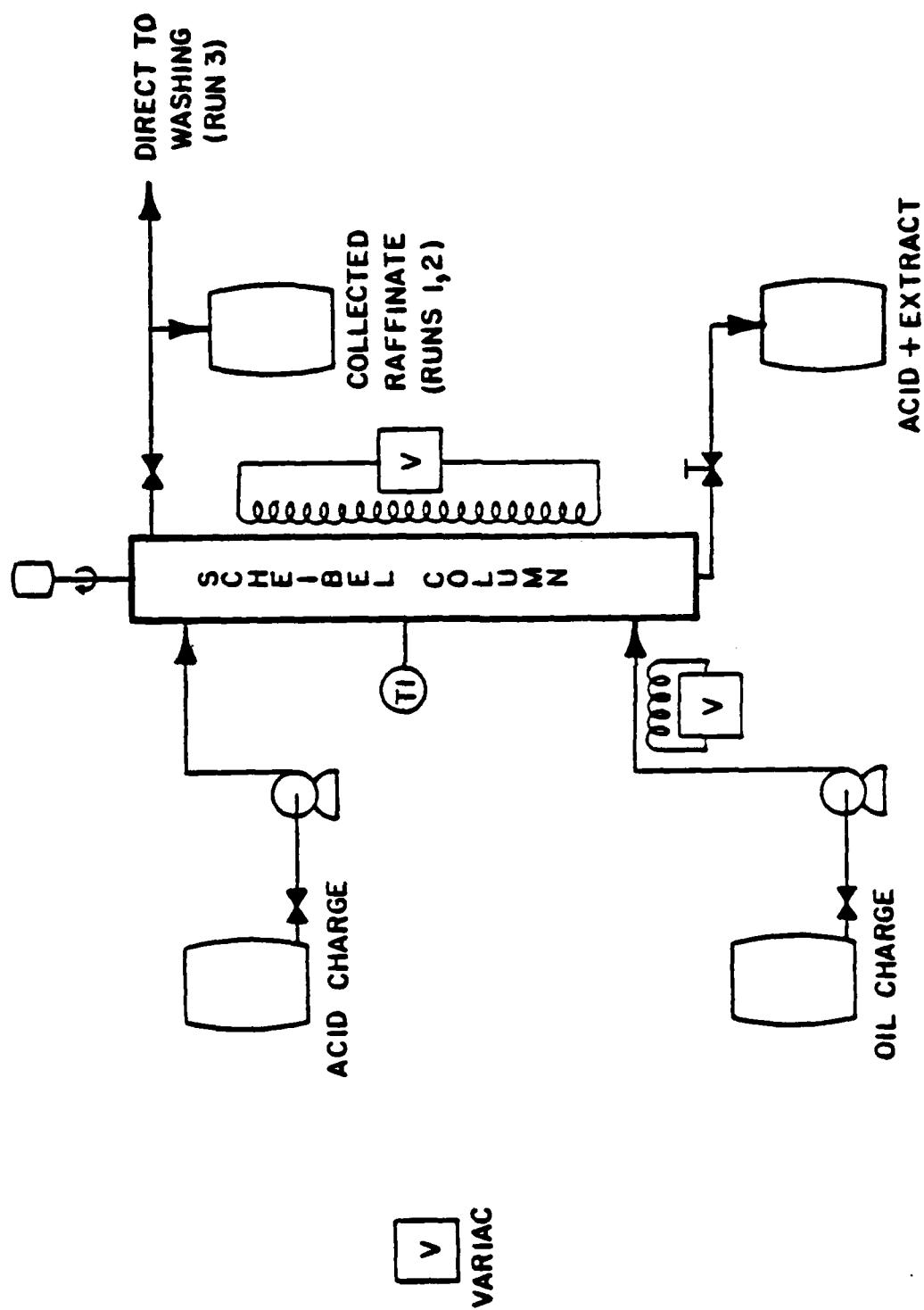


Figure 16. Acid Extraction

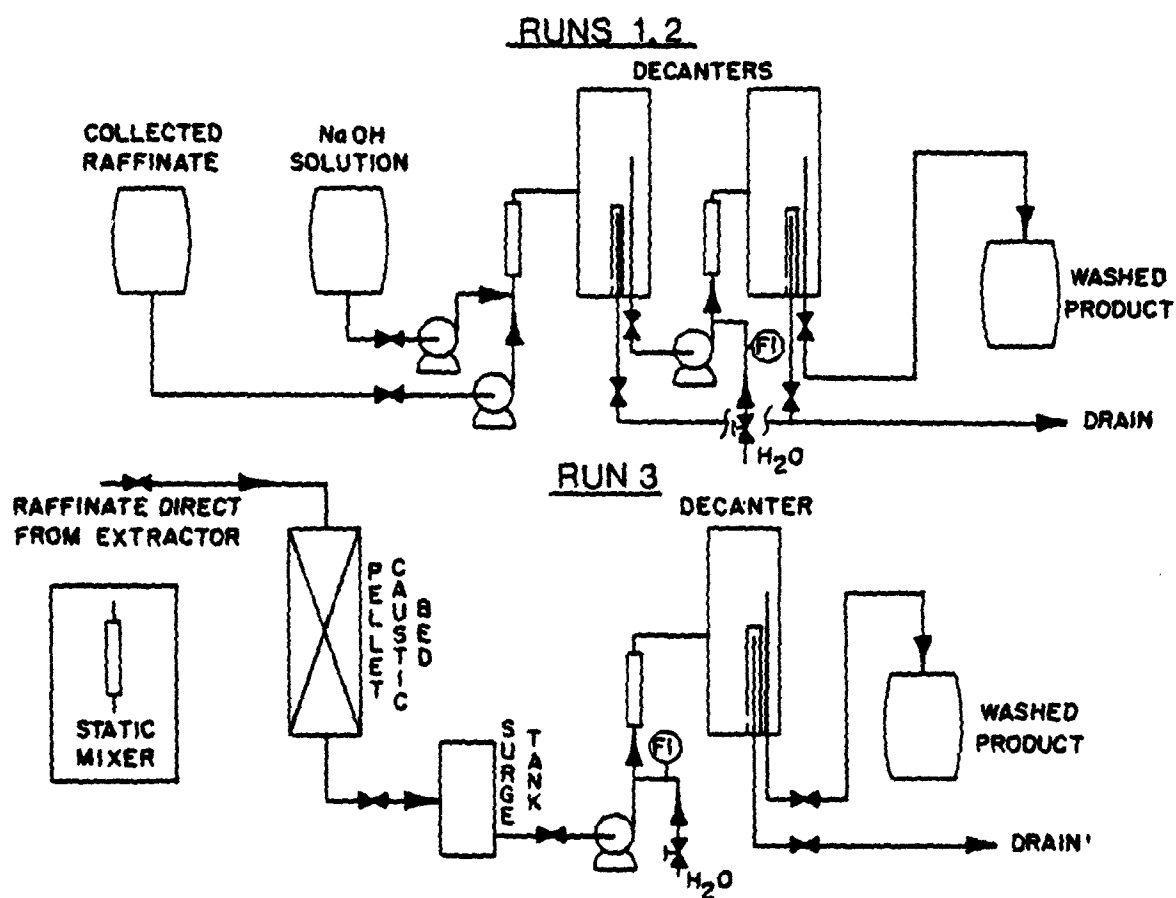


Figure 17. Raffinate Washing

through a bed of pelletized sodium hydroxide and then water washed. In-line static mixing elements were used in both procedures to increase the efficiency of liquid phase contacting.

3. CHEMICAL DESCRIPTION

The mineral acid employed was obtained from a commercial source and diluted with water to produce a solution of nominally 41% (weight) acid. Identification of the specific mineral acid used is withheld for proprietary reasons. The sodium hydroxide solution was prepared by dissolving sufficient commercial sodium hydroxide in water to produce a solution containing 870 ppm NaOH.

4. FEEDSTOCKS

The feedstocks for this operation consisted of the stripper overhead from the CSHT operation and the <600°F fractionator overheads from both the CSHT and MRCC operation. These feedstocks were blended to provide the combinations of converted (MRCC) and straight run (CSHT) components as indicated in Table 29. These feed blends are characterized in greater detail in the experimental section.

5. EXPERIMENTAL/RESULTS

The extraction conditions used and the properties of the feed and extractor raffinate are shown in Tables 30, 31, and 32. The reader should note that the product for run 3

(Continued on page 105)

TABLE 29
ACID EXTRACTION - FEEDSTOCK BLENDS

EXTRACTOR RUN NO.	WT % DISTILLATES FROM:	
	<u>CSHT</u>	<u>MRCC</u>
1	100	0
2	68	32
3	0	100

TABLE 30
ACID EXTRACTION - RUN-1

OPERATING CONDITIONS				
COMPOSITE NO.	1	2	3	4
AVERAGE OIL CHARGE RATE, LB FT ⁻² HR ⁻¹	537.9	495.5		
AVERAGE ACID CHARGE RATE, LB FT ⁻² HR ⁻¹	83.8	75.3		
AVERAGE TEMPERATURE NEAR INTERFACE, °F	115	112		
AVERAGE ACID STRENGTH, WT %	41	41		
AVERAGE CHARGE RATIO, OIL/ACID, WT/WT	6.66	6.58		

FEED AND PRODUCT INSPECTIONS								
ITEM	FEED				PRODUCTS			
COMPOSITE NO.	1	2	3	4	1	2	3	4
API	36.2	35.4			37.9	37.1		
BROMINE NO.	12.8	15.0			11.5	12.8		
SULFUR, WT %	0.02	0.02			0.02	0.02		
BASIC NITROGEN, WT %	0.78	0.83			0.17	0.20		
BASIC NITROGEN REMOVED, %	-	-			78.2	75.9		
DISTILLATION, D2887-73, °F								
IBP	269	301			262	297		
5 WT %	354	471			350	371		
10 WT %	393	482			390	410		
50 WT %	505	545			508	523		
90 WT %	591	604			586	595		
95 WT %	604	621			598	605		
EP	620	633			631	621		
HYDROCARBON REMOVED, %					7.9	11.5		

TABLE 31
ACID EXTRACTION - RUN-2

OPERATING CONDITIONS									
COMPOSITE NO.	1		2		3		4		
AVERAGE OIL CHARGE RATE, LB FT ⁻² HR ⁻¹	383.4		354		422.8		454.4		
AVERAGE ACID CHARGE RATE, LB FT ⁻² HR ⁻¹	61.2		55.2		63.7		75.1		
AVERAGE TEMPERATURE NEAR INTERFACE, °F	114		117		117		118		
AVERAGE ACID STRENGTH, WT %	45		42		43		42		
AVERAGE CHARGE RATIO, OIL/ACID, WT/WT	6.26		6.41		6.64		6.95		
FEED AND PRODUCT INSPECTIONS									
ITEM	FEED				PRODUCTS				
COMPOSITE NO.	1	2	3	4	1	2	3	4	
API	(36.2)	36.9	36.0	35.8	34.5	38.6	37.6	37.7	
BROMINE NO.	(31.0)	31.0	31.0	31.0	32.0	36.0	33.0	32.0	
SULFUR, WT %	(0.04)	0.04	0.03	0.04	0.03	0.04	0.04	0.04	
BASIC NITROGEN, WT %	(0.77)	0.77	0.63	0.69	0.12	0.16	0.17	0.09	
BASIC NITROGEN REMOVED, %	-	-	-	-	-	79.2	73.0	87.0	
DISTILLATION, 02807-73, °F									
IBP	(165)	165	173	179	165	168	176	190	
5 WT %	(260)	260	271	269	257	260	270	272	
10 WT %	(311)	311	322	322	300	306	319	320	
50 WT %	(481)	481	485	491	481	481	484	489	
90 WT %	(574)	574	576	583	578	575	577	581	
95 WT %	(580)	580	587	603	587	582	592	602	
EP	(674)	674	745	727	705	718	726	692	
HYDROCARBON REMOVED, %	-	-	-	-	11.0	12.6	6.4	9.4	

TABLE 32
ACID EXTRACTION - RUN-3

OPERATING CONDITIONS									
COMPOSITE NO.	1		2		3		4		
AVERAGE OIL CHARGE RATE, LB FT ⁻² HR ⁻¹	433.6								
AVERAGE ACID CHARGE RATE, LB FT ⁻² HR ⁻¹	76.1								
AVERAGE TEMPERATURE NEAR INTERFACE, °F	120								
AVERAGE ACID STRENGTH, WT %	37								
AVERAGE CHARGE RATIO, OIL/ACID, WT/WT	5.70								
FEED AND PRODUCT INSPECTIONS									
ITEM	FEED				PRODUCTS				
COMPOSITE NO.	1	2	3	4	1	2	3	4	
API	37.6				37.4				
BROMINE NO.	71.3				80.4				
SULFUR, WT %	0.04				0.04				
BASIC NITROGEN, WT %	0.38				0.02				
BASIC NITROGEN REMOVED, %	-				94.7				
DISTILLATION, D2887-73, °F									
IBP	131				143				
5 WT %	192				200				
10 WT %	221				230				
50 WT %	374				387				
90 WT %	551				548				
95 WT %	578				572				
EP	612				605				
HYDROCARBON REMOVED, %	-				9.9				

is a final washed product since in-line caustic contacting and water washing were employed.

The raffinates from runs 1 and 2 were washed in off-line equipment, and the properties of the washed raffinates are shown in Table 33. Caustic washing was carried out by contacting the raffinate with an equal volume of caustic solution containing 870 ppm NaOH at approximately 110°F. It should be noted that only three washed raffinate composite samples were analyzed from extractor run 2.

A portion of the acid extract phase from extractor run 2 was neutralized and the resultant oil layer separated, washed, and dried. The characterizations obtained on this hydrocarbon product are shown in Table 34. A material accounting summary for this operation will be found in Section XI, Table 61.

6. DISCUSSION

As seen by comparing the data listed in Tables 30, 31, and 32, dilute mineral acid extraction removes the majority of the basic nitrogen compounds without significant changes in either sulfur content or bromine number. The bromine number, not surprisingly, varies directly with the level of converted (MRCC) component in the feedstock. The high distillation endpoints seen in Tables 30 and 31 may reflect the addition of CSHT stripped overhead and represent only the last 2% of the distillation.

TABLE 33
WASHED RAFFINATE PROPERTIES

ITEM	RESULTS						
	1-1	1-2	2-1	2-2	2-3		
EXTRACTOR RUN-COMPOSITE NO							
API	37.7	37.3	38.0	37.5	37.1		
SULFUR, WT %	0.02	0.02	0.03	0.04	0.04		
NITROGEN, WT %	0.31	0.33	0.34	0.35	0.34		
BASIC NITROGEN, WT %	0.15	0.15	0.10	0.12	0.11		
HYDROGEN, WT %	13.1	13.5	13.1	13.1	13.1		
BROMINE NUMBER	13.2	13.5	36.2	35.9	37.0		
RAMSBOTTOM CARBON, WT %	0.15	0.16	0.28	0.26	0.10		
DISTILLATION, D2887(WT%N ^o F)							
IBP	286	277	173	180	193		
5	370	363	259	269	278		
10	410	406	306	318	325		
50	529	517	485	484	490		
90	604	589	579	577	586		
95	617	601	589	589	602		
EP	636	655	662	655	657		
OVERALL RECOVERY, WT% FEED	89.5			88.5			

TABLE 34

ACID EXTRACTION - EXTRACT PROPERTIES

°API	12.8
Elemental Analysis, Dry Basis, Wt. %	
Carbon	80.49
Hydrogen	10.07
Sulfur	0.11
Nitrogen	7.21
Oxygen	1.22
Water, Wt. % As Tested	6.4
Gross Heating Value, Btu/lb	15749
Bromine Number	35.8
Distillation, D2887	
IBP	321
5	374
10	401
20	440
50	514
80	567
90	587
95	600
EP	828

It should also be noted that the washing operation accounts for an average of 4.5% denitrogenation as shown by Tables 30, 31, and 33.

Except for the last composite of run 2, and for run 3, basic nitrogen removals were generally slightly less than anticipated on the basis of Phase II results. Analysis of extractor operating data and results was carried out to determine the causes of this problem, and the results of our analysis are shown in Figure 18 where the experimentally observed denitrogenation values are plotted against those predicted by the derived regression equation. The diagonal line is a hypothetical ideal correlation line rather than a specific fit of the data. The magnitude of the coefficients of the derived equation clearly indicates that the acid/oil ratio is the predominant variable. It should be noted that the data point representing run 3 was corrected to the extractor basis value for input into analysis. In spite of the inherent scatter of the input data, the derived expression appears to give good correlation with the observed data, and points out the need for maintaining a proper acid/oil ratio.

7. CONCLUSIONS

- Acid extraction is successful in removing the majority of the basic nitrogen compounds of both straight run and cracked shale oil distillates.

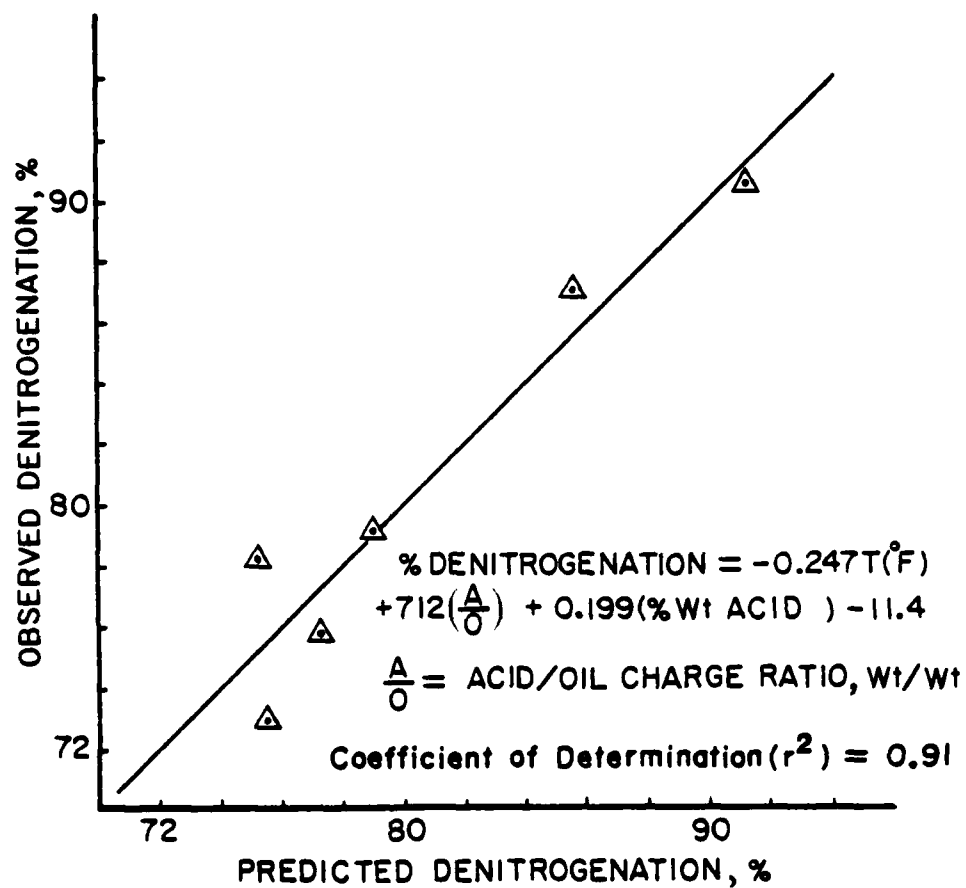


Figure 18. Correlation Of Variables In Acid Extraction

- Maintaining a proper acid/oil ratio is very important in achieving maximum basic nitrogen removal.

SECTION VI
RECYCLE OIL HYDROTREATING

1. OBJECTIVE

The objective of recycle oil hydrotreating (COHT) is to provide an upgraded MRCC >600°F recycle oil stream for charging to the MRCC unit or for use as a lowered nitrogen and sulfur content fuel oil component.

2. MECHANICAL DESCRIPTION

The recycle oil hydrotreater, Figure 19, was the same reactor system as that employed in the crude shale hydrotreating operation (Section III) with the following exceptions.

- A. The guardcase charge of activated alumina was replaced with inert 1/4-1/2" alumina balls and functioned as a supplementary charge preheater.
- B. The catalyst was a commercial nickel/molybdate instead of cobalt/molybdate.
- C. Alumina balls, 1/4-1/2", replaced the tabular alumina chips used in the preheat and postheat sections.
- D. Only one liquid product was removed from the reactor. Stripper overhead, where produced, was recombined with the bottoms product of the stripper.

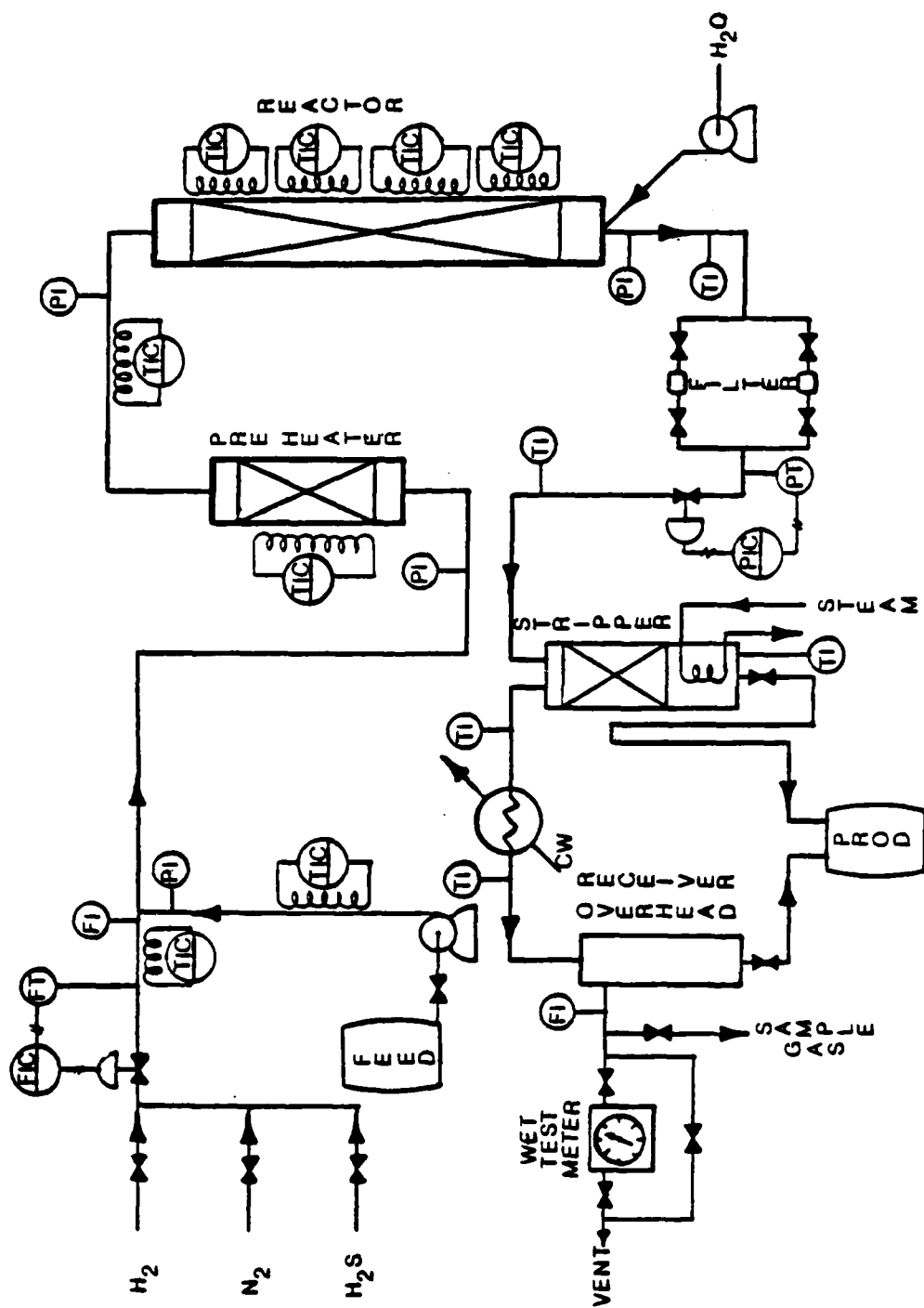


Figure 19. Recycle Oil Hydrotreater

3. CATALYST

The catalyst for this operation was a commercial nickel/molybdate in the form of 1/16" extrudates.

4. FEEDSTOCK

The feedstock used was a portion of the >600°F fractionator bottoms from MRCC run 1 (100% virgin CSHT bottoms feedstock).

5. EXPERIMENTAL

The commercial nickel/molybdate catalyst was sandwiched between 5" layers of 1/4"-1/2" inert alumina balls, and the reactor pressure checked to 1300 psig using nitrogen, then hydrogen. After correction of leaks the catalyst was sulfided as described in Section III. On completion of sulfiding, the reactor was cooled in flowing hydrogen to approximately ambient temperature. The reactor was pressurized to the desired operating level and the gas rate set. The reactor was preheated to approximately 300°F, feed was started, and the reactor was brought up to the desired operating temperature.

6. RESULTS

The major problem encountered during this operation was plugging of the catalyst bed and pressure control valve with a particulate material believed to be sulfided catalyst fines.

The reaction conditions employed and the mass and hydrogen balanced component yield structure obtained are shown in Table 35. Properties of the feedstock and product composite samples are shown in Table 36.

A material accounting for this operation is shown in Table 60, along with the MRCC summary.

7. DISCUSSION

Sulfur and nitrogen removals appear similar to those obtained during Phase II at comparable operating conditions.

As a lowered sulfur and nitrogen residual fuel, the reaction product meets or exceeds all specifications except pour point. This deficiency could be corrected with the appropriate pour depressor or by addition of light fractions such as LCO to produce an excellent fuel oil blending component.

As discussed in Section IV, the reaction product from this operation also serves as an upgraded feedstock for modified reduced crude conversion. It should be reemphasized, however, that the reaction product must be processed through the MRCC unit on a blocked out basis to achieve the maximum benefits of hydrotreating.

The relatively short run time precluded any estimation of catalyst aging for this operation.

TABLE 35
RECYCLE OIL HYDROTREATING
CONDITIONS AND YIELD STRUCTURE

AVERAGE CONDITIONS

TEMPERATURE, °F	675
PRESSURE, PSIG	1430
LHSV (Hr ⁻¹)	0.99
GAS CHARGE, SCFB	5515
HYDROGEN, Vol%	81.2
CATALYST	COMMERCIAL Ni/Mo

YIELD STRUCTURE

(Wt% FEED NORMALIZED TO 100%)

H ₂ O 0.04	C ₄ 0.96
H ₂ S 0.04	C ₅ 0.03
NH ₃ 1.17	C ₅ 0.80
H ₂ -1.10	LIQUID 96.33
C ₁ 0.02	HYDROGEN CONSUMPTION, SCFB 660
C ₂ 1.08	CLOSURE 100.2%
C ₃ 0.63	

TABLE 36

COHT FEED AND PRODUCTS

ITEM	FEED		PRODUCTS	
	1	2	1	2
COMPOSITE NO.				
API	23.5	23.5	26.2	25.9
NITROGEN, WT %	1.08	0.96	0.69	0.52
BASIC NITROGEN, WT %	0.47	0.48	0.33	0.31
SULFUR, WT %	0.06	0.05	0.01	0.01
HYDROGEN, WT %	11.9	12.1	12.5	12.9
OXYGEN, WT %	0.09	0.09	0.07	0.06
RAMSBOTTOM CARBON, WT %	0.73	0.65	0.64	0.64
IRON, PPM	4	8	6	5
NICKEL, PPM	<1	1	1	<1
VANADIUM, PPM	<1	1	1	1
ARSENIC, PPM	1	<1	<1	<1
DISTILLATION, D2887, (WT%)(°F)				
IBP	554	599	451	328
5	603	620	575	371
10	619	631	603	609
50	732	734	711	719
90	887	877	865	881
95	928	909	899	920
EP	979	944	942	952
VISCOSITY, cSt				
100°F	-	-	29.00	24.90
210°F	-	-	4.37	4.56
POUR, °F	-	-	+75	+75

SECTION VII

GUARDCASE HYDROTREATING

1. OBJECTIVE

The objective of guardcase hydrotreating is to reduce the nitrogen, sulfur, olefin, and metallic contaminant levels to the point that they will not interfere with subsequent catalytic processing. A commercial nickel/molybdate catalyst was employed in this process.

2. MECHANICAL DESCRIPTION

The reactor used for guardcase hydrotreating, Figure 20, was identical to that used in the crude shale and recycle oil hydrotreating except for the final product washing step. The liquid products from the stripper (overhead + bottoms) were collected in a surge tank and pumped with an equal volume of water through a static mixing section to a decanter. The water layer was discarded and the decant oil collected and dried to <10 ppm water by circulation through an off-line fixed bed of 3-A molecular sieve (not shown on Figure 20).

3. CATALYST DESCRIPTION

The catalyst was a commercial nickel/molybdate catalyst, initially in the form of 1/16" extrudates. In an effort to improve liquid-catalyst contacting, the catalyst was crushed and screened to yield a catalyst mix which averaged 1/16" in diameter x 1/16" long. This charge was blown free of dust using dry compressed air prior to charging.

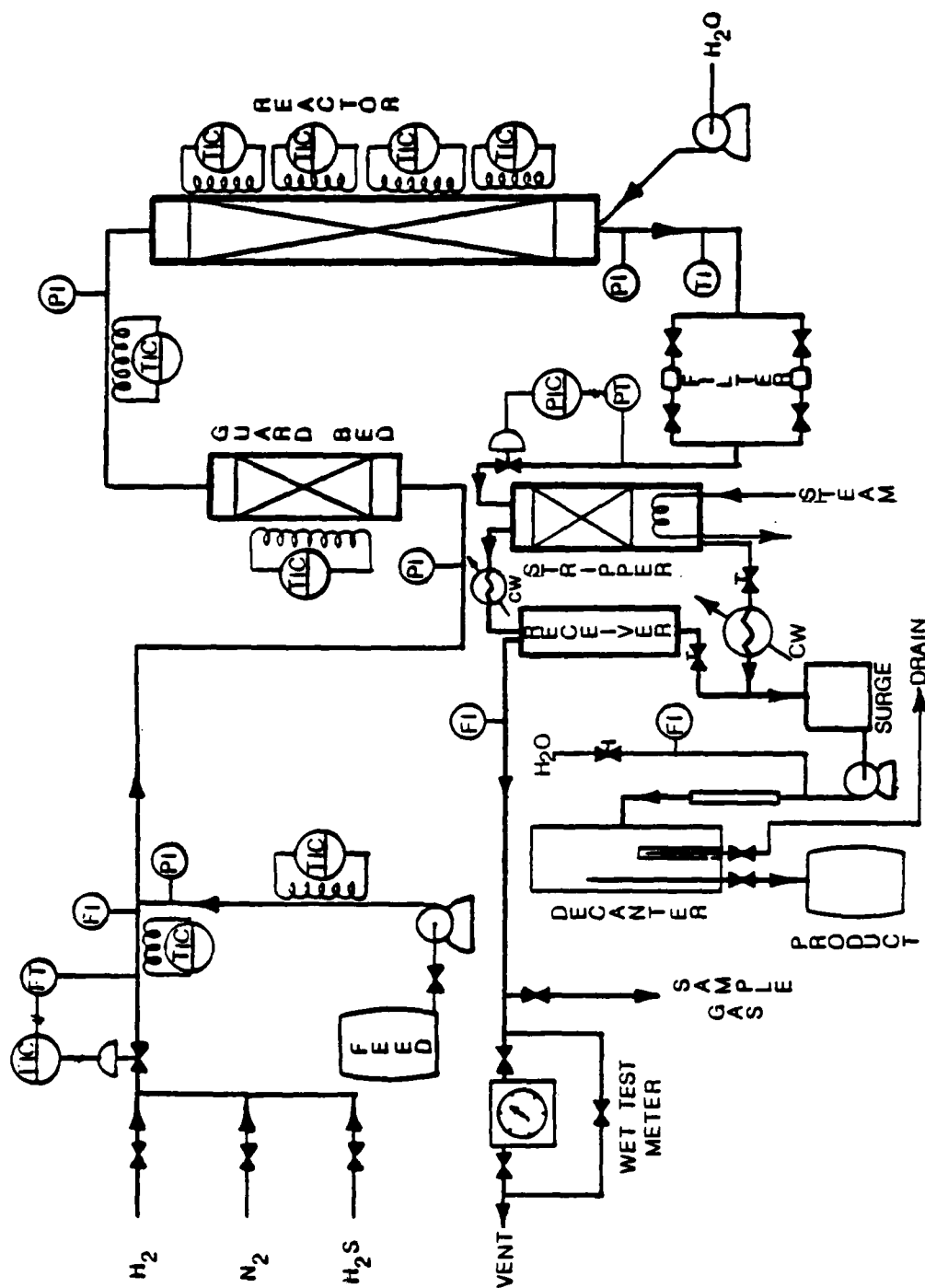


Figure 20. Guardcase Hydrotreater

4. FEEDSTOCKS

The feedstocks for guardcase hydrotreating were the washed raffinates from acid extraction (Section V). The selection of the specific raffinates to be further processed to turbine fuel was made on the basis of the boiling ranges of the raffinates, and the boiling ranges of the final desired turbine fuel samples. The raffinate from extractor run 2, produced from the feedstock containing 68% straight run (CSHT) and 32% converted (MRCC) distillates was selected for processing to form the JP-8 sample pool. The raffinate from extractor run 3, produced from 100% converted (MRCC) distillates, was selected for processing to form the majority of the JP-4 sample pool. This selection of raffinate charge based on boiling range was intended to minimize the time and cost of fractionation required to produce the final turbine fuel samples. Because of its boiling range, and because of time considerations, the raffinate from extractor run 1, produced from 100% straight run (CSHT) distillates, was not further processed to turbine fuel.

5. EXPERIMENTAL

As in previous catalyst loadings, a 3" layer of 1/4"-1/2" alumina balls was used to support the catalyst bed and to act as a post reaction section. The hydrotreating catalyst, 0.99 gallon, was charged in a manner proprietary to Ashland Oil. A 3" section of 1/4"-1/2" alumina balls was

charged at the top of the catalyst bed to serve as a preheat and initial liquid distribution section.

The catalyst was sulfided by heating the catalyst charge from ambient temperature to 700°F in flowing 100% H₂S at atmospheric pressure. Temperature increases during sulfiding averaged 100°F per hour after the initial exotherm. When the temperature had stabilized at 700°F, the system was pressurized to full bottle pressure (approximately 130 psig) and held for one hour. The reactor was then cooled to ambient temperature in flowing hydrogen, the operating pressure and desired gas rate set, and the reactor heated to approximately 300°F for starting liquid feed.

A fresh catalyst charge was used for both the JP-8 and JP-4 pool hydrotreating. Charging and sulfiding operations were essentially identical in both cases.

Conditions were monitored continuously and recorded at hourly intervals to reflect all pertinent pressures, temperatures, and flows. The primary reaction controls were the sulfur and nitrogen content of the reaction product, and conditions were adjusted to achieve <1 ppm levels of the elements in the final product.

6. RESULTS

The predicted start-up conditions were:

Temperature	650°F
Pressure (total)	1250 psig
LHSV	1.0
Gas Circulation	4000 SCFB (100% H ₂ basis)

These conditions failed to produce products having the desired product sulfur and nitrogen levels with either raffinate charge. In the interest of processing time and cost, the off-specification products, produced during adjustment to the finally acceptable conditions, were combined with the material produced during the weekly start-up and shut-down periods and fractionated using the equipment shown in Figure 3. The <400°F overhead was reprocessed through the guardcase hydrotreater, and the product was used as a JP-8 pool reforming charge component. The >400°F fractionator bottoms were characterized as a diesel fuel blending component. All recycle from the JP-4 pool processing was reprocessed through the guardcase hydrotreater. The combined product (recycle + one pass) was fractionated in the equipment shown in Figure 3, and the bottoms subjected to an additional laboratory fractionation to produce a combined overhead of approximately 90% (weight) of the guardcase product. This combined overhead, having an endpoint more suitable for JP-4

use, served as the feedstock for JP-4 pool reforming. The bottoms from the laboratory fractionation were characterized as a second diesel fuel blending component.

On-specification products from both sample pools were dried to <10 ppm H₂O by recirculation through a 3-A molecular sieve, and were chlorided to 7 ppm by addition of carbon tetrachloride.

The major problems encountered during this operation included the fluctuations in refinery hydrogen composition (mentioned during previous sections) and the problems imposed by the budgetary requirement for weekend shutdown of the unit. The first problem was addressed by using inlet and off-gas analyses as point estimators for the average value as was done in previous units involving hydrogen processing. Where hydrogen contents of the liquid streams were available, both mass and hydrogen balancing were used to obtain the hydrogen consumption.

The operating conditions and yield structures obtained in processing the components of the JP-8 sample pool are given in Table 37. The yield structures shown are both mass and hydrogen normalized. The properties of the charges and products are shown in Table 38. It should be noted that the nitrogen and sulfur levels shown in this table are not typical of the <1ppm values produced at process conditions shown

TABLE 37

**JP-8 POOL GUARDCASE HYDROTREATING
CONDITIONS AND YIELD STRUCTURE**

<u>Feedstock</u>	<u>Extractor Run 2 Raffinate</u>	<u><400°F Recycle</u>
Conditions:		
Temperature, °F	699	730
Pressure, psig	1400	1400
LHSV (Hr ⁻¹)	0.69	0.79
Gas Circ. Rate, SCFB	5650	5966
H ₂ Content, Vol. %	77.8	77.5
Yield Structure (Normalized to 100% Feed):		
H ₂ O	0.21	0
H ₂ S	0.04	0
NH ₃	0.41	0
H ₂	-1.02	-0.81
C ₁	0.27	0.51
C ₂	0.95	0.90
C ₃	0.95	2.00
C ₄	0.36	1.12
C ₅	0.02	0.69
>C ₅	3.49	4.94
Liquid	94.31	90.63
Closure	99.2	97.6
Hydrogen Consumption, SCFB	560	420

TABLE 38

**JP-8 POOL GUARDCASE HYDROTREATING
FEED AND PRODUCT PROPERTIES**

<u>Item</u>	<u>Feedstocks</u>		<u>Products</u>	
	<u>Raffinate</u>	<u>Recycle</u>	<u>One Pass</u>	<u>Recycle</u>
API Gr.	37.5	46.9	41.4	47.8
Nitrogen, (ppm)	3400	71	3	<1
Sulfur, (ppm)	340	12	1	<1
Oxygen, Wt. %	0.197	(0)	(0)	(0)
Hydrogen, Wt. %	13.1	13.67	13.74	14.10
Bromine Number	36.4	-	0.4	-
Distillation, D2887, (Wt. %) (°F)				
IBP	132	161	194	185
5	269	226	279	240
10	316	241	320	259
50	486	347	464	337
90	581	406	572	419
95	593	414	580	442
EP	658	430	659	576

in Table 37, but resulted from a unit upset during the final hours of operation where off-specification product was accidentally collected. The properties of the JP-8 pool recycle fractionation charge and products are shown in Table 39. As previously mentioned, the overhead was rehydrotreated and used as a component of the JP-8 reforming feed while the fractionation bottoms were characterized as a diesel fuel blending component.

The conditions used in the guardcase hydrotreating of the JP-4 pool are shown in Table 40, together with the yield structures obtained. Recycle processing was rather extensive and accounted for approximately 60% of the final product. In the yield structures shown, only the total pool was hydrogen balanced, as well as mass balanced.

The parenthetical entries for the one pass raffinate processing were calculated using data for the total pool and recycle processing. The properties of the raffinate charge and the total product pool are shown in Table 41. The properties and relative yields of fractions obtained during fractionation of the JP-4 guardcase product are given in Table 42. The combined overheads from the pilot plant fractionation and laboratory fractionation provided the

TABLE 39

**JP-8 POOL GCHT RECYCLE FRACTIONATION
CHARGE AND PRODUCT PROPERTIES**

<u>Item</u>	<u>Charge</u>	<u>Overhead</u>	<u>Bottoms</u>
Wt. % (Recovery Basis)	100	29.1	70.9
API, Gr.	41.0	46.9	37.6
Nitrogen, ppm	300	71	360
Sulfur, ppm	25	12	50
Distillation, D2887, Wt. %, °F			
IBP	171	161	410
5	283	226	425
10	323	241	439
50	470	347	508
90	547	406	580
95	588	414	591
EP	700	430	700

TABLE 40

**JP-4 POOL GUARDCASE HYDROTREATING
CONDITIONS AND YIELD STRUCTURE**

<u>Item</u>	<u>Raffinate One Pass</u>	<u>Recycle One Pass</u>	<u>Total Pool</u>
Feedstock			
Temperature, °F	730	730	729
Pressure, psig	1400	1400	1400
LHSV, (hr ⁻¹)	0.7	0.8	0.5
Gas Circulation Rate, SCFB	7320	6620	6920
H ₂ Content, Vol. %	72.4	78.0	76.4
Yield Structure, Wt. % Feed (Normalized to 100%)			
H ₂ S	(0.04)	0	0.04
NH ₃	(0.41)	0	0.41
H ₂	(-2.01)	-0.83	-2.84
C ₁	(0)	0	0
C ₂	(0)	0.24	0.07
C ₃	(3.70)	4.51	4.21
C ₄	(0.81)	1.04	0.95
C ₅	(0.17)	0.24	0.21
<C ₅	(12.54)	1.15	6.21
Liquid	(84.34)	93.65	90.73
Closure, Wt. %	(101.0)	101.1	101.0
Hydrogen Consumption, SCFB	(1100)	433	1553

(Calculated from total pool and recycle data)

TABLE 41

JP-4 POOL GUARDCASE HYDROTREATING
FEED AND PRODUCT PROPERTIES

<u>Item</u>	<u>Raffinate Feed</u>	<u>Total JP-4 Product</u>
API, Gr.	38.4	42.5
Nitrogen, ppm	3400	2
Sulfur, ppm	400	3
Hydrogen, Wt. %	12.00	14.08
Bromine Number	80.4	0.5
Distillation, D2887		
IBP	132	165
5	167	235
10	229	256
50	380	390
90	556	532
95	583	601
EP	602	637

TABLE 42
JP-4 POOL GCHT PRODUCT FRACTIONATION

	<u>Charge</u>	<u>Fractionator Overhead</u>	<u>Laboratory Overhead</u>	<u>Combined Overhead</u>	<u>Bottoms + Undistilled</u>
Wt. % Recovery Basis	100	54.7	32.8	87.5	12.5
API Gravity	42.5	54.7	35.7	44.8	38.2
Nitrogen, ppm	2	<1	1	1	20
Sulfur, ppm	3	<1	<1	1	7
Bromine Number	0.5	-	-	0.4	-
Distillation,	D2887	D86	D86	D2887	D86
IBP	165	227	421	156	442
5	235	255	432	227	460
10	256	264	437	243	467
50	390	311	484	344	527
90	532	360	496	467	570
95	571	370	508	499	580
EP	637	377	516	547	603

% H₂ on combined overhead = 13.39

chargestock for JP-4 pool reforming. The laboratory bottoms, combined with the approximately 14% of the pilot plant bottoms which were not distilled, were characterized as a diesel fuel blending component.

A summary of material accounting for this operation will be found in Section XI, Table 62.

7. DISCUSSION

The increase in the severity of processing conditions, over those predicted from Phase II work, which was required to produce acceptable product nitrogen and sulfur levels, is believed to be due to the lower hydrogen feed partial pressure available for Phase III hydrotreating, and to lower quality of the raffinate feedstock caused by lower nitrogen removals. In larger scale operations, this would be readily corrected by minor adjustments and optimization of operating conditions.

The differences in the processing severities required for the two charge pools may be due to the significantly greater olefin content of the JP-4 pool chargestock with the attendant competitive reactions for an already lowered hydrogen supply.

The relatively short run times for this operation and the requirement for weekend shutdowns preclude any reasonable estimate of catalyst life.

SECTION VIII

REFORMING

1. OBJECTIVES

In the EXTRACTACRACKING process the primary objective of reforming is freeze point modification of the guardcase hydrotreater product to meet jet fuel specifications, with octane improvement of the gasoline fraction of the reformat being a secondary objective.

This application of reforming is believed to be unique and novel. The boiling range of the shale derived feedstock which we processed ($>600^{\circ}\text{F}$ E.P.), and the atypical operating conditions ($800\text{--}925^{\circ}\text{F}$, 3-10 LHSV, 500-600 psig, and a H_2 charge rate of 3000-4000 SCFB) are significantly different from those of usual reformer chargestocks and operating conditions. To our knowledge, this is the first time the reforming of such stocks has been attempted for the purpose of freeze point depression, and especially for freeze point depressions of such magnitude.

2. MECHANICAL DESCRIPTION

The reactor configuration used in reforming is shown in Figure 21, and was identical to the configuration used in recycle oil hydrotreating, Figure 19, with the following exceptions:

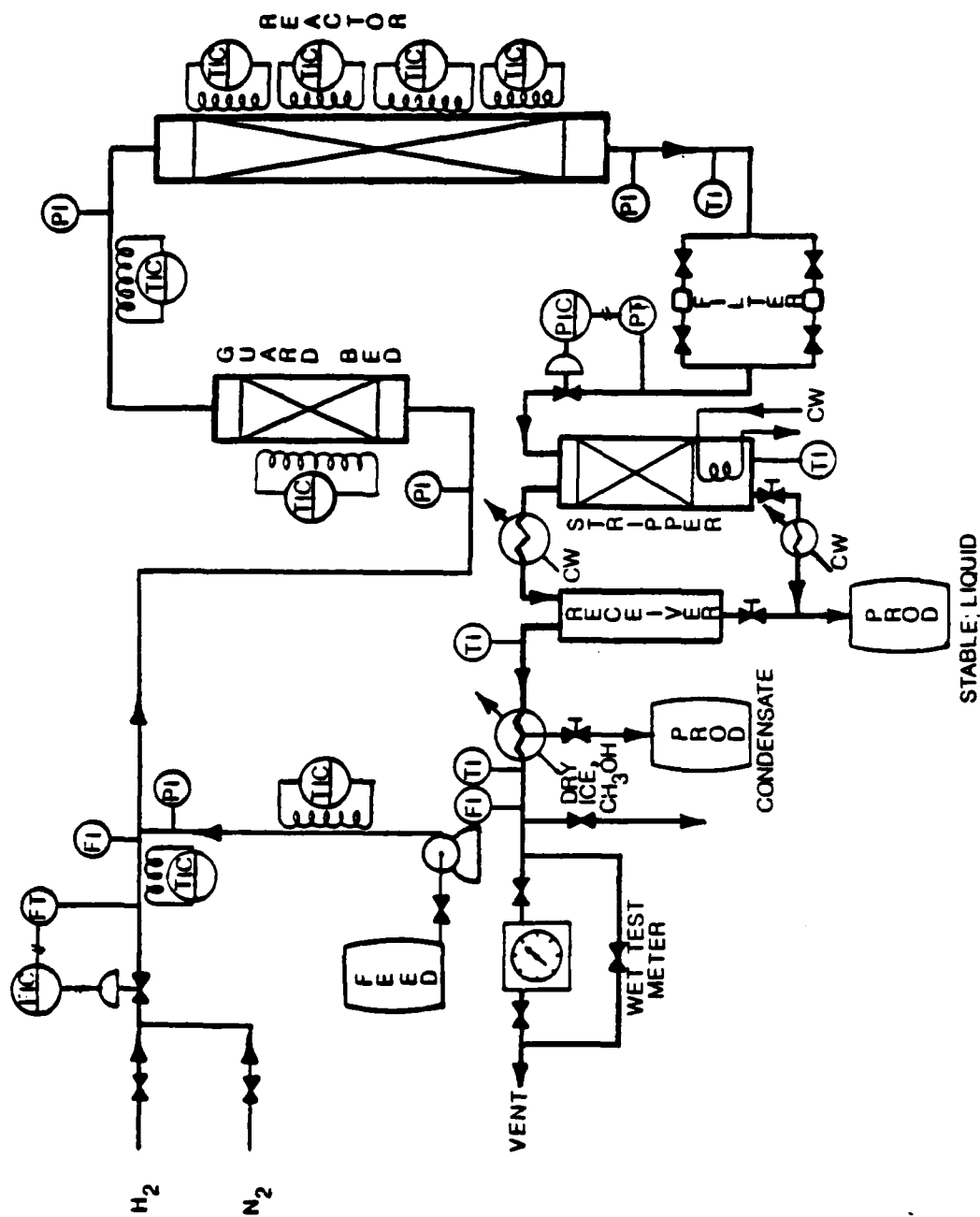


Figure 21. Reformer

- A. Cold water was passed through the coil on the stripper bottoms instead of steam as in previous units.
- B. A modified Heliflow condenser coil, immersed in a dry ice/methanol bath was inserted in the off-gas line from the stripper overhead accumulator to condense and collect light liquids present in the off-gas stream.
- C. Water injection at the reactor outlet was not employed.

The condensate from the off-gas line condenser was retained separately in a cold storage cabinet and used as a component in the final JP-4 pool without further catalytic processing. All other liquid products from the reactor were combined for subsequent aromatic saturation.

3. CATALYST DESCRIPTION

The catalyst employed in this operation was a commercially available bimetallic Pt/Re reforming catalyst in the form of 1/16" extrudates. Because of the highly endothermic nature of the reaction, the catalyst was charged using semi-logarithmic dilution with tabular alumina chips.

4. FEEDSTOCKS

Feedstocks for the JP-8 pool were the guardcase reactor products from the processing of washed extractor run 2 raffinate, and the guardcase product resulting from processing

of the <400°F overhead obtained by fractionation of the off-specification guardcase product. These feedstocks were not blended prior to reforming to capitalize on the savings of time and cost obtained by processing the <400°F overhead at a higher LHSV.

The feedstock for the JP-4 pool consisted of the combined JP-4 guardcase reactor product fractionated to improve the boiling range as described in the previous section.

5. EXPERIMENTAL

A 3" layer of 1/4"-1/2" alumina balls was charged to the reactor to support the average catalyst bed and to serve as a postheat section. The six catalyst charges, diluted with inert tabular alumina chips as specified by pseudologarithmic dilution, were individually well mixed and charged to the reactor, catalyst concentration in the zones decreasing from bottom to top of the reactor. A 5" layer of 1/4"-1/2" alumina balls completed the charge.

To preclude the possibility of liquid hydrocarbons contacting the catalyst during prereduction, the preheaters were purged with nitrogen at 450°F for one hour prior to cooling and reconnecting to the charged reactor. Bottled hydrogen was employed in prereduction to further preclude hydrocarbon contamination.

The reactor was pressure checked to 700 psig using nitrogen and then hydrogen. After correcting leaks, the reactor pressure was set at atmospheric and the hydrogen rate set at 20-25 SCFH. The reactor was heated from ambient temperature to 925°F at a rate of 100°F per hour. When the average bed temperature reached 925°F, the reactor was pressurized to 600 psig and held for one hour in flowing hydrogen. The reactor was then cooled to ambient temperature using refinery hydrogen.

Separate catalyst charges were used for reforming the JP-8 and JP-4 pool charges. The volumes of active catalyst used for these charges were 0.197 gallon and 0.206 gallon, respectively. Catalyst loading and prereduction were as described above.

In start-up of the reactor, the desired pressure and gas rate were set, and the reactor heated to an average temperature close to the desired operating temperature. Feed was started and the feed rate adjusted to the desired value. The temperature of the reactor was then adjusted so that the average bed temperature corresponded to the desired operating temperature. No effort was made to impose temperature equality on all zones.

All temperatures, pressures, and flows were monitored continuously and recorded on an hourly basis. The primary control for the reaction was product freezing point, and conditions were adjusted as required to maintain the desired level of freezing point depression.

A sample of JP-4 reformat product was fractionated in the laboratory to produce a gasoline sample.

6. RESULTS

The major problems encountered in reforming included, as in previous units, the problems associated with a variable composition of the refinery hydrogen stream used, and the catalyst deactivation observed in JP-8 pool processing which required conditions of increasing severity to maintain the desired freezing point depression. Budgetary restrictions which required weekend shutdown also contributed to the operating problems by creating recycle processing requirements.

The conditions used and the product results obtained in processing the two JP-8 pool feedstocks are given in Table 43, together with the corresponding feedstock properties. These feedstocks are characterized more completely in Section VII. The average conditions used and the corresponding yield structures obtained for processing the JP-8 pool feedstocks are shown in Table 44 and are both mass and hydrogen normalized to 100%. Gas line condensate was included in the liquid

TABLE 43
REFORMING JP-8 POOL

DATE	TIME	FEEDSTOCK	CONDITIONS						RESULTS			
			TEMP °F	PRESS PSIG	LHSV HR ⁻¹	GAS CHARGE SCFB	H ₂ MOLE %	FREEZING POINT °F	S	O	A	
-	-	Spec. GCHT	-	-	-	-	-	-18.4	76.5	1.1	22.4	
5/4/81	1000	"	873	500	3.7	4240	-	-46	-	-	-	
5/4/81	1200	"	893	480	3.7	4240	-	-90*-	-	-	-	
5/5/81	0830	"	885	500	4.4	5767	76.4	-90-	49.1*	0.9*	50.0*	
5/6/81	0800	"	889	500	4.4	5767	76.4	-67.9	53.6	1.0	45.4	
5/7/81	0800	"	889	500	4.4	5767	76.4	-66.1	57.5	0.8	41.7	
5/8/81	0800	"	889	500	4.4	5767	76.4	-58.0	54.1	1.1	44.8	
5/11/81	1115	"	900	600	4.5	4119	72.6	-65.2	47.5	1.3	51.2	
5/12/81	0800	"	900	600	4.5	4119	72.6	-67.0	48.4	1.3	50.3	
5/13/81	0800	"	900	600	4.4	4119	87.1	-57.1	-	-	-	
5/13/81	1215	"	912	600	4.4	4128	87.1	-61.6	42.5	1.4	56.1	
5/14/81	0800	"	915	600	4.4	4128	81.9	-50.8	53.1	3.1	43.8	
-	-	-400°F RECYCLE	-	-	-	-	-	-68.8	82.6	2.3	15.1	
5/15/81	0800	"	922	600	9.8	4855	80.0	-90-	70.0	0.4	29.6	

*Includes Off-Gas Condensate

TABLE 44

JP-8 POOL REFORMING

CONDITIONS AND YIELD STRUCTURE

<u>Feedstock</u>	<u>On Specification GCHT Product</u>	<u><400°F Recycle</u>
Average Conditions:		
Temperature, °F	900	922
Pressure, psig	600	600
LHSV (Hr ⁻¹)	4.5	9.8
Yield Structure, Wt. % Feed Normalized to 100%		
H ₂	1.13	0.44
C ₁	2.00	0.42
C ₂	0.81	0.88
C ₃	1.83	1.17
C ₄	0.05	0.31
C ₅	0.14	0.42
>C ₅	5.24	3.10
Liquid	88.81	93.26
Hydrogen Production, SCFB	608	230
Closure	99.6	98.8

weight percent shown. The conditions used in JP-4 pool reforming and some of the properties of the feedstock and reactor products are shown in Table 45. A more complete feedstock characterization was given in Section VII. In contrast to JP-8 pool reforming, the conditions used in reforming of the JP-4 pool were steadily decreased in severity in an effort to obtain a product having a freeze point of higher than -90°F .

The yield structure, normalized to 100%, obtained at the most severe processing conditions, is shown in Table 46. Yield structure calculations for the other sets of processing conditions were precluded because of the absence of reliable gas analyses.

A sample of the JP-4 pool reformat, produced at 880°F , 5.0 LHSV, 495 psig, was fractionated in the laboratory to yield a gasoline blending component. The off-gas condensate was blended with the fractionator overhead and yielded 81.4 LV % on a reformat charge basis. Properties of this gasoline fraction will be given in Section X. The properties of the total blended reformer products and of the off-gas condensate are shown in Table 47. The reader should note that the combined JP-8 pool includes the -400°F recycle product. The off-gas condensate averaged 10% weight of the total reformat product.

TABLE 45

JP-4 POOL REFORMING

FEED AND PRODUCT PROPERTIES

	<u>Feed</u>	<u>Products</u>			
Day	-	5/26/81	5/27/81	5/27/81	5/28/81
Time	-	1700	0800	1300	0800
Conditions:					
Temperature, °F	-	880	880	850	827
Pressure, psig	-	495	495	495	495
LHSV, (Hr ⁻¹)	-	5.0	6.1	6.1	6.3
Gas Charge, SCFB	-	3751	4413	4432	4372
H ₂ , Mole %	-	75.9	75.9	-	76.6
Results:					
Freezing Point, °F	-73.3	-90	-90	-90	-81.3
FIA Analysis:					
S	73.7	35.4	38.1	42.6	49.1
O	0.9	0.3	0.8	1.2	0.5
A	25.4	64.3	61.1	56.2	50.4

TABLE 46
JP-4 POOL REFORMING YIELD STRUCTURE

Conditions:

Temperature, °F	880
Pressure, psig	495
LHSV, Hr ⁻¹	5.0

Yield Structure:

H ₂	2.29
C ₁	1.13
C ₂	4.54
C ₃	2.95
C ₄	0.89
C ₅	3.32
<C ₅	0.32
Liquid	84.55

Hydrogen Production, SCFB	1230
Closure	99.2

TABLE 47
REFORMING - FINAL BLENDED POOL PROPERTIES

Item	JP-8	JP-4	Condensate
API Gr.	39.6	37.8	
Freezing Point, °F	-63.4	-90-	-90-
FIA Analysis:			
S	55.6	47.0	87.9
O	1.0	0.8	2.2
A	43.4	52.2	9.9
Hydrogen, Wt. %	12.63	12.11	-
Distillation:	D-86	D-86	D2887
IBP	204	236	-14
5	266	274	-6
10	302	348	22
50	382	366	191
90	524	480	296
95	558	506	323
100	582	544	402

A material accounting summary for this operation will be found in Section XI, Table 63.

7. DISCUSSION

The declining catalyst activity observed during reforming of the JP-8 pool is ascribed to the abnormally high nitrogen and sulfur levels which were introduced during the upset during the final hours of guardcase hydrotreating. This deactivation would not be anticipated during normal operation. The yield structure shown for the "on-specification" GCHT product reforming represents the median processing conditions for this stream.

The reader will note that reforming for freeze point depression was not required for the JP-8 <400°F recycle stream, or for the JP-4 guardcase product because of their already acceptable freezing points. Reforming of these streams was carried out to provide products whose molecular structure reflected the changes, other than normal paraffin rearrangements, which occur during reforming. The relatively severe conditions used in the initial reforming of the JP-4 pool were chosen to enhance the octane level of the gasoline fraction.

The relatively short run lengths, combined with the requirement for weekend reactor shutdown, precluded any reasonable estimate of catalyst life for this operation.

It will be noted that hydrogen production observed during the reforming operation parallels the hydrogen consumption data obtained during guardcase hydrotreating of the various streams. It should also be noted that the guardcase hydrotreater is normally considered as an integral feature of reforming and not as a separate operation.

SECTION IX
AROMATIC SATURATION

1. OBJECTIVES

The objectives of this operation were:

- A. To reduce the aromatics content of the reformat to levels acceptable for the various types of turbine fuels, and,
- B. To manufacture products with varying aromatics content up to a maximum level of 35%, it being anticipated that the higher BTU content (per gallon) of the higher aromatics content fuels represents a possible trade-off with engine performance and engine life.

In the succeeding pages of this report, a fuel having an aromatics level intentionally higher than the specifications for the given fuel type will be referred to as Broadrange.

Ashland also contemplates the manufacture of a new jet fuel type having an expanded boiling range, as well as an increased aromatics level.

2. MECHANICAL DESCRIPTION

The hydrotreater configuration used in this operation is shown in Figure 22. The gas and liquid reactants, initially heated in small preheaters, are mixed and passed in concurrent up-flow through a common preheater containing 1/4"-1/2" alumina balls. The heated gas liquid mixture passes in downflow mode through a reactor having a nominal diameter of 3.1", which is charged with a pseudologarithmically diluted bed of a commercial nobel metal hydrotreating catalyst and tabular alumina chips. The packed bed length was approximately 84", and a 3" layer of 1/4"-1/2" alumina balls at the top and bottom of the bed serve as distribution and bed support sections, respectively.

The combined gas and liquid product flow through a back pressure control valve, and the combined stream, at essentially atmospheric pressure, then passes successively through a water cooled condenser and a liquid-gas disengager cooled using an off-site chilled methanol recirculation system. The liquid product is collected for further processing and the off-gas vented.

3. CATALYST

The catalyst used in this operation was a commercially available Pt/Al hydrogenation catalyst in the form of 1/32" extrudates. Because of the highly exothermic nature of the

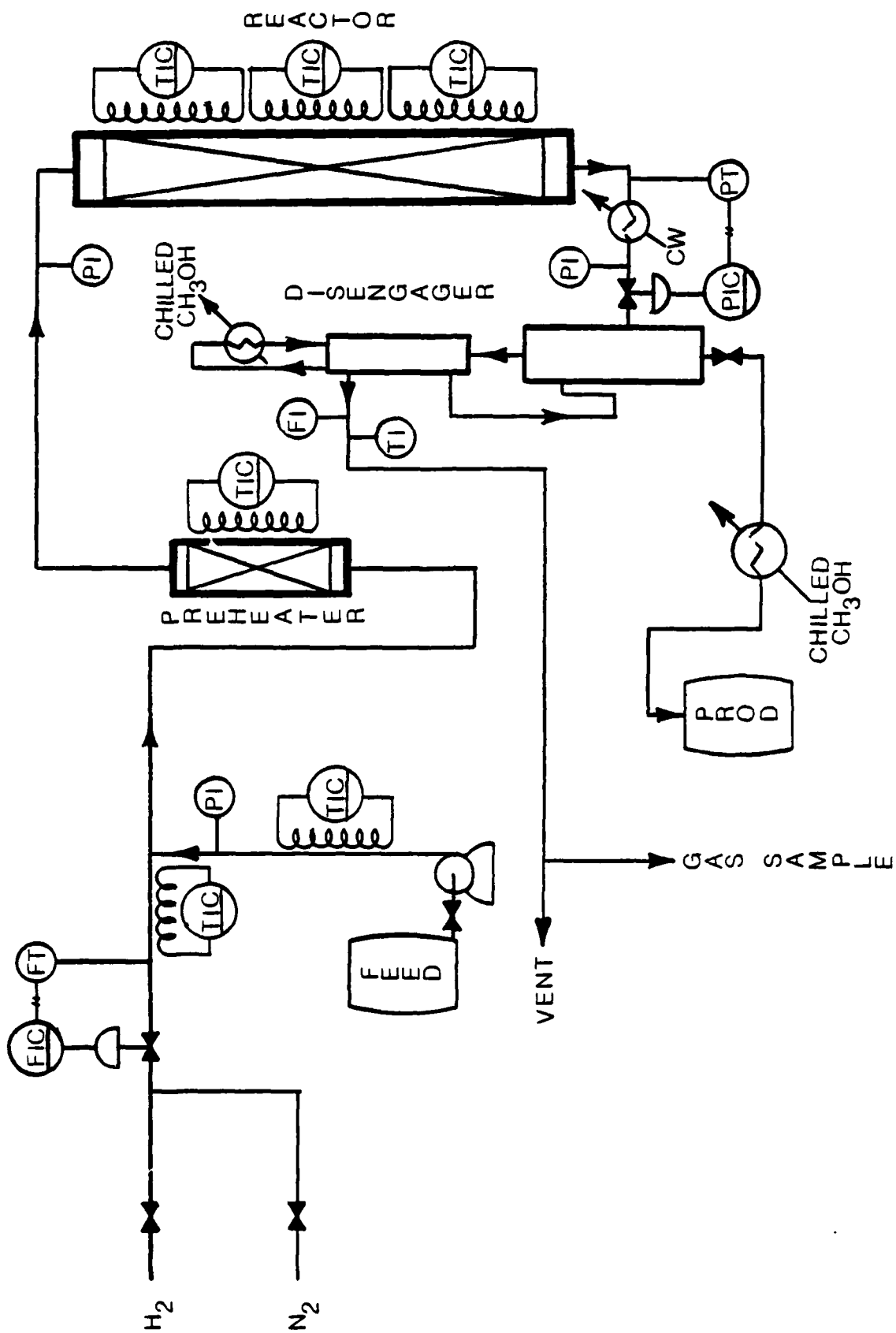


Figure 22. Aromatic Saturation Reactor

reaction, the catalyst was charged using pseudologarithmic dilution with tabular alumina chips. It should be noted that cobalt/molybdate or nickel/molybdate catalysts could also be employed, undiluted, in this operation as is done in some commercial solvent hydrotreating units.

4. FEEDSTOCKS

The feedstocks for this operation were the reformates from the JP-8 and JP-4 pool processing which are characterized in Section VIII.

5. EXPERIMENTAL

The reactor was charged with a 3" layer of 1/4"-1/2" alumina balls to serve as a bed support and as a postheat section. The six logarithmically diluted catalyst charges were added, in order, to the reactor. The concentration of active catalyst increased from top to bottom of the bed, and the total volume of active catalyst was 0.73 gallons.

The reactor was pressure checked with nitrogen and then hydrogen, and leaks corrected. A bottle hydrogen supply was attached to the reactor to prevent contacting of the catalyst with hydrocarbons during pre-reduction. The reactor was vented to atmospheric pressure, and the hydrogen rate set at 20-25 SCFH. The reactor was heated from ambient temperature to an average bed temperature of 750°F at a rate of 100°F per hour. Once the average bed temperature stabilized

at 750°F, the system pressure was increased to 300 psig while maintaining hydrogen flow, and held for one hour at these conditions. The reactor was cooled to ambient temperature using refinery hydrogen, and the desired pressure and gas rate set. The reactor system was preheated to approximately 350°F and feed started and adjusted to the desired value. The system was adjusted until the desired operating conditions were obtained. All temperatures, pressures, and flows were monitored continuously and recorded hourly. Inlet and off-gas samples were taken every eight hours.

Two products were produced from the JP-8 pool feedstock: a product meeting JP-8 turbine fuel aromatic specifications and an experimental product which has a maximum aromatics level of 35%. This experimental sample has been designated as a Broadrange JP-8.

Both of the JP-8 type products were fractionated using the equipment shown in Figure 3, in atmospheric mode, to stabilize the flash point of the bottoms product to JP-8 specifications. The bottoms product from each of the two samples constituted the final turbine fuels; the overhead from the stabilization furnished an additional component for blending in the final JP-4 turbine fuel.

The JP-4 sample was processed at one set of conditions only, and the product from the reaction was blended with the stabilization overhead (above) and with the previously described off-gas condensate from the reforming operation to produce the JP-4 turbine fuel. This final sample was sparged with nitrogen to stabilize the Reid vapor pressure and acid number prior to submission.

Two catalyst charges were used in these operations. The first charge did not perform as anticipated because of apparent contamination from the previous reactor feed, which persisted after an extensive cleanout, and which was released from the reactor walls at pre-reduction temperatures. Because of time and budgetary considerations, the use of this catalyst charge was continued in the production of the Broadrange JP-8 sample. A fresh catalyst charge, loaded and pre-reduced as discussed above, was used in the saturation of the JP-8 and JP-4 samples.

6. RESULTS

The conditions used, and the mass and hydrogen normalized yield structures obtained for the JP-8 and JP-8 Broadrange saturations are shown in Table 48. The properties of the JP-8 pool feed, the stabilized bottoms, and the stabilization overhead obtained with the JP-8 and JP-8 Broadrange samples are shown in Table 49. A more complete characterization of the stabilized bottoms for these two samples will

TABLE 48

**JP-8 POOL AROMATIC SATURATION
CONDITIONS AND YIELD STRUCTURE**

	<u>JP-8</u>	<u>Broad Range JP-8</u>
Temperature, °F	553	550
Pressure, psig	550	500
LHSV, Hr ⁻¹	1.93	1.92
Gas Charge, SCFB	10,667	9,626
Hydrogen Content, Vol. %	80.2	77.5
Yield Structure, Wt. % Cg Normalized to 100%		
H ₂	-1.67	-1.05
C ₁	0	0
C ₂	0	0.06
C ₃	0.33	0.89
C ₄	1.22	0.17
C ₅	0.62	0.51
Liquid	99.49	99.42
Hydrogen Consumption, SCFB	907	570
Closure, %	99.0	101.9

TABLE 49

**JP-8 POOL AROMATIC SATURATION
FEED AND PRODUCT PROPERTIES**

<u>Type</u>	<u>Feed</u>	<u>Stabilized Product</u>		<u>Overhead From Stabilization</u>
		<u>JP-8</u>	<u>JP-8 Broadrange</u>	
°API	39.6	41.3	39.7	61.9
FIA Analysis				
S	55.6	79.8	65.7	87.5
O	1.0	0.9	0.5	0.5
A	43.4	19.3	33.8	12.0
Tag Flash Point, °F	Room Temp.	114	116	Room Temp.
Distillation, °F				
Type	D86	D86	D86	D2887
IBP	204	319	312	2
10	302	348	344	134
20	333	360	362	166
50	412	409	410	226
90	524	507	510	262
EP	582	547	562	294

be found in Section X where the properties of the final samples are reviewed. The reader should note that the overheads from the JP-8 and JP-8 Broadrange were collected as one sample and characterized. The overhead fraction from the stabilization was approximately 8% weight of the total combined fractionation charge. The distillation points shown correspond to the specification and reporting points for JP-8 turbine fuels.

The conditions used and the hydrogen and mass normalized yield structure obtained in processing the JP-4 reformat are shown in Table 50. The properties of the feed and saturation product are shown in Table 51, together with the properties of the final blended JP-4 sample. The final blended sample will be more completely characterized in Section XI.

Freezing points of the aromatic saturation products for the JP-8 pool samples were -65°F prior to stabilization, while the freezing point of the reformat charge was -63.4 . Similar negligible changes were observed in Phase II. A material accounting summary for this operation will be found in Section XI, Table 64.

TABLE 50

JP-4 POOL AROMATIC SATURATION
CONDITIONS AND YIELD STRUCTURE

Temperature, °F	556
Pressure, psig	550
LHSV, Hr ⁻¹	1.93
Gas Charge, SCFB	10,912
Hydrogen Content, Vol. %	77.9
Yield Structure, Wt. % Feed Normalized to 100%	
H ₂	-2.35
C ₁	0
C ₂	0
C ₃	0.04
C ₄	0.45
C ₅	0.66
Liquid	101.2
Hydrogen Consumption, SCFB	1290
Closure, %	99.4

TABLE 51

**JP-4 POOL AROMATIC SATURATION
FEED AND PRODUCT PROPERTIES**

	<u>Feed</u>	<u>Saturation Product</u>	<u>Blended* Product</u>
°API	37.8	44.7	49.5
FIA Analysis			
S	47.0	88.1	88.0
O	0.8	0.7	1.0
A	52.2	11.2	11.0
Distillation, °F			
Type	D2887	D2887	D86
IBP	113	119	120
5	223	217	-
10	244	246	210
50	362	365	304
90	493	473	438
95	524	498	-
EP	665	548	496
*Composition Wt. %			
Off-Gas Condensate from Reformer			10.0
stabilization Overhead from JP-8 Pool			18.4
JP-4 Saturation Product			71.6

7. DISCUSSION

The higher hydrogen consumption of the JP-4 charge parallels the higher than anticipated hydrogen consumption obtained in guardcase hydrotreating and the high hydrogen production rates obtained during reforming. Much of the higher hydrogen consumption observed in the aromatic saturation of the JP-4 sample was due to the high aromatics content of the feedstock, some of which was formed, by intent, in the reforming step.

SECTION X
FINAL SAMPLE CHARACTERIZATIONS

1. OBJECTIVE

This section details the chemical and physical properties of the fuel samples submitted to the Air Force as part of the requirements of Phase III.

2. SOURCE OF CHARACTERIZATION DATA

Turbine fuel specification tests were carried out by the Ashland Jet Fuel Laboratory. Properties of the remaining samples were determined by the Analytical Group of Ashland Petroleum R&D, with assistance from Ashland's Automotive and Product Application Laboratory.

3. RESULTS

The results of the specification testing of the turbine fuel samples are shown in Tables 52, 53, and 54 for the JP-4, JP-8, and JP-8 Broadrange samples, respectively. A blending summary for these fuels is included in Section XI, Table 65.

The origin and characterization of the diesel fuel blending component samples are shown in Tables 55 and 56. Characterization values obtained by evaluation of the gasoline fraction and residual fuel fraction are shown in Tables 57 and 58.

TABLE 52

JP-4 TURBINE FUEL
INSPECTION RESULTS

ITEM	METHOD	APPEARANCE	RESULTS				SPEC LIMIT	PRODUCT NAME
10	D156	Color (Saybolt)		+	3	0	Report	Jet Fuel
28		Visual/BC = Bright/Clear - CL = Cloudy	B	C			Report	
COMPOSITION								GRADE
100	D974	Acidity, Total (mg KOH/g)	•	0	0	5	0.015 max	JP-4
110	D1319	Aromatics (vol %)	1	1	•	0	25.0 max	LABORATORY PERFORMING TESTS
120	D1319	Olefins (vol %)	1	•	0		5.0 max	Ashland Jet Fuel
130	D1219	Sulfur, Mercaptan (wt %)	•				0.001 max	Laboratory
140	D484	Doctor Test (p.p.m., negative) *	N				Negative	REPORT DATE
150	D1266	Sulfur, Total (wt %)	•	0	0	7	0.40 max	6-25-81
VOLATILITY								COMPLIES WITH SPECIFICATION
200	D86	Distillation Initial BP (F)	1	2	0		Report	<input type="checkbox"/> YES <input type="checkbox"/> NO
205	D86	10% Rec (F)	2	1	0		Report	CONTRACT NUMBER
210	D86	30% Rec (F)	2	4	1		293 max	ORDER NUMBER
215	D86	50% Rec (F)	3	0	4		374 max	DATE SAMPLED
220	D86	90% Rec (F)	4	3	8		473 max	6-25-81
225	D86	95% Rec (F)						SAMPLE NUMBER
230	D86	Final BP (F)	4	9	6		518 max	RDA
235	D86	Residue (%)	1	•	0		1.5 max	BATCH NUMBER
240	D86	Loss (%)	1	•	0		1.5 max	6407B
245	D86	Recovery at 400 F (%)			•			YANK NUMBER
250	FTMS 1151	Explosiveness (vol %)						FINAL PRODUCT
260	•	Flash Point (F)						QUANTITY U. S. GALLONS
270	D287	Gravity, API (60F)	4	9	•	5	45.0-57.0	
280	D1298	Gravity, Specific (60/60 F)	•	7	8	1 3	.802-.751	
290	D123	Vapor Pressure (lb Reid)	2	•	9		2.0-3.0	
FLUIDITY								SAMPLING LOCATION
300	D2386	Freezing Point (F)		-	9	0	-72 max	ASHLAND OIL, INC.
310	D445	Viscosity (cSt)			•			PILOT PLANT
COMBUSTION								DESTINATION
400	D1405	Antiknock-Gravity Product	6	3	4	9	5250 min	
410	D3338	Net Heat of Combustion (Btu/lb)	1	8	6	4 7	18400 min	
420	D1740	Luminometer Number						
430	D1323	Smoke Point	2	4	•	2	20.0 min	REMARKS
440	D1840	Naphthalenes (vol %)		•				*JFTOT at 500°F
450	D1655	Smoke-Volatility Index			•			
CORROSION								Gravity, API
500	D158	Copper Strip (2 h at 212F)	1	B			1b max	Top
510	IP227	Silver Strip						Mid
STABILITY								Btm
600	D1241	Color & P (mm Hg)		0	•	0	25 max	
610	D1241	Color Tube Color Code		1			<3	
CONTAMINANTS								FSII, Vol. 2
700	IP225	Copper Content (mg/kg)						Top
710	D381	Existent Gum (mg/100 ml)	0	•	8		7.0 max	Mid
720	D2276	Particulates (mg/liter)	0	•	1		1.0 max	Btm
730	D1094	Water Reaction Vol Change (ml)		0	•	5	1 max	
740	D1094	Water Reaction Ratings		1		A	1b max	
750	D2358	WSSM	1	0	0		70 min	Spun Deposit Rating 0
ADDITIVES								
800	Anti-icing (vol %)		•				0.10-0.15	
810	Antioxidant (lb/M Btu)			•			6.0 min	
820	Corrosion Inhibitor (lb/M Btu)				•		3.0-6.0	
830	Metal Deactivator (lb/M Btu)			•				
840	Antistatic, ppm			•				
OTHER TESTS								APPROVED BY (Typed name and signature)
900	D2624	Conductivity (CU)						
910	D2276A2	Filtration Time, Minutes					15 max	

* Alternate Methods. Record Method Used.

DO FORM (Proposed)

TURBINE FUEL TEST REPORT

TABLE 53

JP-8 TURBINE FUEL
INSPECTION RESULTS

PROPERTY	SPECIFICATIONS	RESULTS
Color, Saybolt	Report	+26
Total Acid Number, mg KOH/gm	0.015 max.	0.009
Aromatic, vol. percent	25.0 max.	19.3
Olefins, vol. percent	5.0 max.	0.9
Sulfur, Mercaptan, wt. percent	0.001 max.	0.0005
Sulfur, total, wt. percent	0.3 max.	0.012
Distillation Temperature, °F		
Initial Boiling Point	Report	319
10 percent recovered	401 max.	348
20 percent recovered	Report	360
50 percent recovered	Report	409
90 percent recovered	Report	507
End Point	572 max.	547
Residue, vol. percent	1.5 max.	1.0
Loss, vol. percent	1.5 max.	1.0
Flash Point, °F	100 min.	114
Gravity, deg. API	37-51	41.3
Density, kg/l at 15°C	0.775-0.840	0.8185
Freezing Point, °F	-58 max.	-60.7
Viscosity, at -4°F, centistokes	8.0 max.	5.62
Net Heat of Combustion, Btu/lb	18,400 min.	18,536
Combustion		
(1) Hydrogen Content, wt percent or	13.5 min.	
(2) Smoke Point, mm or	25 min.	
(3) Smoke Point, mm and	19 min.	19.3
Naphthalenes, vol. percent	3.0 max.	0.27
Copper Strip Corrosion, 2 hr. at 212°F	No. 1b max.	1b
Thermal Stability		
Change in pressure drop mm Hg.	25 max.	0.0
Heater tube deposit visual rating	code 2 max.	1
Existent Gum, mg/100ml	7 max.	1.0
Particulate Matter, mg/liter	1.0 max.	0.1
Water Reaction		
Interface Rating	1b max.	1A
Water Separation Index, modified	*	92
Fuel System Icing Inhibitor, vol. percent	0.10-0.15	

* The minimum water separation index, modified, rating for JP-8 shall be 85 with all additives except the corrosion inhibitor and the electrical conductivity additive or 70 with all additives except the electrical conductivity additive.

TABLE 54

BROADRANGE JP-8 TURBINE FUEL

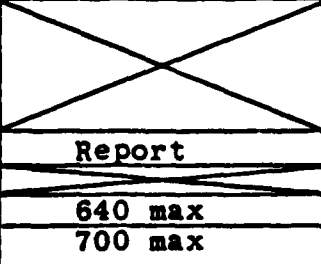
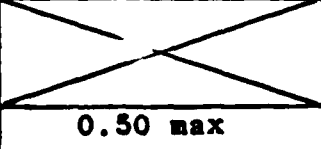

INSPECTION RESULTS

PROPERTY	SPECIFICATIONS	RESULTS
Color, Saybolt	Report	+20
Total Acid Number, mg KOH/gm	0.015 max.	0.009
Aromatic, vol. percent	25.0 max.	33.8
Olefins, vol. percent	5.0 max.	0.5
Sulfur, Mercaptan, wt. percent	0.001 max.	0.0005
Sulfur, total, wt. percent	0.3 max.	0.021
Distillation Temperature, °F		
Initial Boiling Point	Report	312
10 percent recovered	401 max.	344
20 percent recovered	Report	362
50 percent recovered	Report	410
90 percent recovered	Report	510
End Point	572 max.	562
Residue, vol. percent	1.5 max.	1.0
Loss, vol. percent	1.5 max.	1.0
Flash Point, °F	100 min.	116
Gravity, deg. API	37-51	39.7
Density, kg/l at 15°C	0.775-0.840	0.8261
Freezing Point, °F	-58 max.	-61.6
Viscosity, at -4°F, centistokes	8.0 max.	5.55
Net Heat of Combustion, Btu/lb	18,400 min.	18,414
Combustion		
(1) Hydrogen Content, wt percent or	13.5 min.	
(2) Smoke Point, mm or	25 min.	
(3) Smoke Point, mm and	19 min.	16.2
Naphthalenes, vol. percent	3.0 max.	0.49
Copper Strip Corrosion, 2 hr. at 212°F	No. 1h max.	1B
Thermal Stability		
Change in pressure drop mm Hg.	25 max.	0.0
Heater tube deposit visual rating	code 2 max.	1
Existent Gum, mg/100ml	7 max.	1.4
Particulate Matter, mg/liter	1.0 max.	0.1
Water Reaction		
Interface Rating	1h max.	1A
Water Separation index, modified	*	88
Fuel System Icing Inhibitor, vol. percent	0.10-0.15	

* The minimum water separation index, modified, rating for JP-8 shall be 85 with all additives except the corrosion inhibitor and the electrical conductivity additive or 70 with all additives except the electrical conductivity additive.

TABLE 55




**DIESEL BLENDING COMPONENT
SOURCE: JP-8 GCHT FRACTIONATION**

PROPERTY	DF-2 SPECIFICATION	SAMPLE
Gravity, °API	Report	37.6°
Flash Point, °F	125 min	212
Cloud Point, °F	*	-6
Pour Point, °F	Report	-10
Viscosity at 100°F, cs	2.0-4.3	2.92
Carbon Residue on 10% Bottoms	0.35 max	.14
Copper Strip Corrosion	3 max	1B
Ash, Wt %	0.01 max	<.01%
Water and Sediment, Wt %	0.01 max	0
Cetane Number (Cetane Index)	45 min -----	45 (51)
Distillation, °F:		
I		453
10		470
30		482
50		496
70		516
90		557
EP		579
Elemental Analyses, Wt %		
Hydrogen		13.55
Nitrogen		.036
Sulfur		.005
Aromatics, Vol %, By		
FIA		28.6
Mass Spec		22.7
Sodium, ppm		<1
Arsenic, ppm		<1

*Cloud point specification varies with month and state. Refer to Federal Specification VV-F-800C for Diesel Fuel.

TABLE 56

**DIESEL BLENDING COMPONENT
SOURCE: JP-4 GCHT FRACTIONATION**

PROPERTY	DF-2 SPECIFICATION	SAMPLE
Gravity, °API	Report	38.2
Flash Point, °F (PM TYPE)	125 min	210°F
Cloud Point, °F	*	+14
Pour Point, °F	Report	+5
Viscosity at 100°F, cs	2.0-4.3	3.12
Carbon Residue on 10% Bottoms	0.35 max	.42
Copper Strip Corrosion	3 max	----
Ash, Wt %	0.01 max	----
Water and Sediment, Wt %	0.01 max	----
Cetane Number (Cetane Index)	45 min -----	---- (57.5)
Distillation, °F:		
I		442
10		467
30		466
50		Report
70		527
90		552
EP	640 max 700 max	570 603
Elemental Analyses, Wt %		
Hydrogen		13.83
Nitrogen		20 ppm
Sulfur	0.50 max	7 ppm
Aromatics, Vol %, By		
FIA		24.1
Mass Spec		----

*Cloud point specification varies with month and state. Refer to Federal Specification VV-F-800C for Diesel Fuel.

TABLE 57

GASOLINE BLENDING COMPONENT
SOURCE: JP-4 REFORMATE

API GRAVITY	44.4	<u>DISTILLATION, D86</u>	
FIA ANALYSIS, LV%		IBP	128
S	47.7	10	250
O	1.1	50	324
A	51.1	90	380
RVP, PSI	3.9	EP	431
EXISTENT GUM (MG/100ML)	39.2		
RON, CLEAR	84.4		
RON, +1cc TEL/GAL	90.0		
RON, +4cc TEL/GAL	96.2		
MON, CLEAR	76.9		
MON, +4cc TEL/GAL	86.9		
NITROGEN	<1PPM		

TABLE 58

RESIDUAL FUEL BLENDING COMPONENT
SOURCE: MRCC BOTTOMS (>600°F)

	<u>Military Specification</u>	<u>Sample</u>
°API	11.5 min	12.3
Flash Pt.	150°F min	230°F+
Viscosity @ 122°F	225 SSU max	110.8 ssu
Pour Point	15°F upper max	+45°F
Carbon Residue	15% max	3.1% Ramsbottom C.
Sulfur	3.5% max	.07%

4. DISCUSSION

All turbine fuels passed the specifications either established or proposed for the respective fuel types. It should be noted that, except for the increased level of aromatics level and the consequent impact of this increased level on the smoke point, the inspections for the JP-8 Broad-range fuel and JP-8 fuel are essentially identical.

The diesel fuel component obtained from fractionation of the off-specification guardcase product, Table 55, passed all DF-2 specifications. The diesel fuel component obtained by fractionation of the JP-4 guardcase product had a carbon residue on 10% outside of the DF-2 specification for this property. This sample would still serve as an excellent blending component.

The properties of the gasoline fraction were close to those predicted on the basis of Phase II results. The low RVP would not be expected in commercial practice because of the improved pressure recovery facilities for light hydrocarbons.

The residual fuel, consisting of the final >600°F material from the MRCC operations, fails to meet the pour point specification as shown in Table 58. This deficiency could be corrected by appropriate blending, or by the use of pour depressors.

SECTION XI
MATERIAL ACCOUNTING

1. OBJECTIVE

The objective of this section is to account for the full range Occidental in situ shale oil consumed during Phase III operations, and for the products and by-products produced.

2. RESULTS

The weight data shown for the process units, especially the net gas recoveries, were obtained from raw balance data and may differ slightly from the data presented in the mass and hydrogen normalized structures shown in the unit modules.

Where applicable, mass data have been reconciled with a recent physical inventory of material remaining on hand (Table 67).

The accounting data for the process units and for final turbine fuel sample blending is shown in Tables 59 through 65. Weights of the diesel, residual, and gasoline samples are summarized in Table 66. The data shown in Table 67 summarizes the results of a physical inventory of material remaining on hand at the pilot plant facility awaiting disposition instructions from the Air Force.

TABLE 59

CRUDE SHALE HYDROTREATER (CSHT)
(All Weights In Pounds)

CHARGE

Raw shale charged in operating periods	21,992.8
Raw shale charged in lineout operations	<u>1,498.1</u>
Raw shale charged in total process	23,490.9

RECOVERY

Sulfide stripper overhead	2,096.4
Fractionator overhead (<600°F)	5,067.5
Fractionator bottoms (>600°F)	13,881.9
Recycle products not reprocessed	738.0
Net gas recovery	<u>869.2</u>
Total	22,653.0 (96.4%)

LOSSES

Handling losses in reaction	198.4
Fractionation losses (handling + non-condensable vapor loss)	<u>639.5</u>
Total	837.9

NET PRODUCTS FORWARD TO EXTRACTION

Sulfide stripper overhead	2,096.4
Fractionation overhead	<u>5,067.5</u>
Total	7,163.9

NET PRODUCTS FORWARD TO MRCC

Fractionator bottoms	13,881.9
Minus sample	<u>20.0</u>
Total	13,861.9

TABLE 60

**MODIFIED REDUCED CRUDE
CONVERSION (MRCC)
(All Weights In Pounds)**

CHARGE FROM CSHT	13,861.9
RECOVERY (ALL RUNS)	
Liquid Products	
<600°F distillate	4,952.6
>600°F bottoms	1,243.2
Gas	
MRCC	2,918.9
COHT	106.7
Coke	<u>1,844.6</u>
Total	11,066.0
LOSSES	
MRCC	
Lineout, start-up, and shutdown when changing feedstocks	1,184.6
Handling	237.1
Filtration	462.5
Fractionation	<u>614.5</u>
Total	2,498.7
TOTAL ACCOUNTABILITY	13,564.7 (97.9%)
NET PRODUCTS FORWARD	
<600°F distillate to extraction	4,952.6
>600°F bottoms to residual fuel	1,243.2

TABLE 61

ACID EXTRACTION
(All Weights In Pounds)

TOTAL DISTILLATES FROM CSHT AND MRCC	12,116.5
TOTAL CHARGED TO EXTRACTION	9,685.5

RECOVERY

Washed Raffinate	8,441.5
Hydrocarbon Extract	841.7
Distillates Not Extracted (on hand)	2,126.0
Sample of Distillate to Synthetic Fuels Group	<u>200.0</u>

Total	11,609.2
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LOSSES

Blending Chargestocks for Extraction	105.0
Losses in Processing	<u>255.0</u>

Total Losses	360.0
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ACCOUNTABILITY (lbs)	11,969.2 (98.8%)
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RAFFINATE FORWARD TO GCHT	8,441.5
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AD-A128 722

REFINING OF MILITARY JET FUELS FROM SHALE OIL PART III
PILOT PLANT SAMPLE PREPARATION(U) ASHLAND PETROLEUM CO
KY F H TURRILL JUL 82 AFWAL-TR-81-2056-PT-3

3/3

UNCLASSIFIED

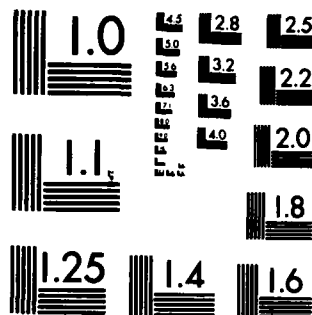
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 62
GUARDCASE HYDROTREATING
(All Weights in Pounds)

JP-8 Pool		JP-4 Pool	
CHARGE		CHARGE	
Raffinate Charged	2767.25	Raffinate Charged	764.7
RECOVERY		RECOVERY	
"Specification" Product	1204.5	Fractionation Overhead	487.5
Reprocessed <400°F Dist.	268.5	to Reformer	
>400°F Diesel Sample	787.0	Fractionation Bottoms	64.8
Recycle not Fractionated	138.0	to Diesel Sample	10.0
Net Gas Loss	270.1	Retained Sample*	179.4
Samples	<u>25.0</u>	Net Gas Loss**	
Total	2693.1		
LOSSES		LOSSES	
Fractionation	36	Fractionation	16.5
RECOVERY + LOSS	2729.1 (98.6%)	RECOVERY + LOSS	758.2 (99.2%)
UNASSIGNED LOSS	38 (1.4%)	UNASSIGNED LOSS	6.5 (0.8%)
JP-8 PRODUCTS TO REFORMING	1473	NET JP-4 TO REFORMER	487.5

* By laboratory

** High gas losses due to high percentage (~60%) of recycle processing required.

TABLE 63
REFORMING
(All Weights in Pounds)

	JP-8 Pool	JP-4 Pool
CHARGE		
JP-8 GCHT Product Forward	1473.0	487.5
Net Charged to Reformer	1441.5	469.5
RECOVERY		
Stable Liquid Product	1186.5	353.0
Off-Gas Condensate	59.0	
Net Gas Loss	123.8	68.5
Samples	15.0	14.5
		2.0
Total	1384.3 (94.0%)	31.5
LOSSES		
GCHT Product Drying and Charging Losses	31.5	469.5
Reactor Leaks* + Unrecovered Condensate	57.2	(96.3%)
Total	88.7 (6.0%)	18.0 (3.7%)
NET PRODUCTS FORWARD		
Stable Liquid to Aromatic Saturation Condensate to JP-4	1186.5 59.0	353.0 14.5

*Leaks repaired prior to JP-4 pool reforming.

TABLE 64

AROMATIC SATURATION (All Weights in Pounds)

JP-8 & JP-8 Broadrange (BR) Pool		JP-4 Pool	
CHARGE		CHARGE	
JP-8 Pool Reformate		JP-4 Reformate	353.5
Forward	1186.5		
Net Charged to Unit	1158.5		
RECOVERY		RECOVERY	
Stabilized Bottoms JP-8*	461.5	Liquid Product	336.0*
Stabilized Bottoms		Gas	0
JP-8(BR)	440.75		
Stabilization Overhead	86.9		
Net Gas Loss	67.9		
Transition Bottoms			
Product**	84.9		
LOSSES		LOSSES	
Handling Loss During		Estimated Loss to JP-8	10.5
Charging	28	Unassigned Loss	7
Fractionation Loss	27		
TOTAL RECOVERY + LOSS	1197*		

*Some mixing of JP-4 and JP-8 occurred during feedstock charge to JP-4 pool.

**Fractionation bottoms removed while changing fractionation charge from JP-8 to JP-8 Broadrange aromatic saturation product.

TABLE 65

TURBINE FUEL BLENDING (All Weights In Pounds)

Components	Weight
JP-4 Aromatic Saturation Product	335
Stabilization Overhead from JP-8 Pool	83.8
Condensate from All Reforming	47.0*
Total	465.8
JP-4 Sample Weight After Blending and N ₂ Sparging	446.0
Loss in Blending and Sparging	19.8
Sample Retained	27.5
Net JP-4 to Air Force	418.5
JP-8 Turbine Fuel Blending	
Stabilized JP-8 From Aromatic Saturation	461.5
Transition Bottoms Material	20.25
Sample Retained	30.5
Net JP-8 to Air Force	451.4
JP-8 Broadrange Turbine Fuel Blending	
Stabilized JP-8 Broadrange from Aromatic Saturation	440.75
Transition Bottoms Material	54.5
Sample Retained	32.25
Net Broadrange JP-8 to Air Force	463

*Some loss of sample occurred during storage.

TABLE 66

**OTHER FUEL SAMPLES
(All Weights In Pounds)**

Diesel Fuel Blending Component From Fractionation of Off-Specification JP-8 Guardcase Hydrotreating Product	603.25
Sample Retained	26.5
 Diesel Fuel Blending Component From Fractionation of JP-4 Guardcase Hydrotreating Product	 58.25
Sample Retained	5.25
 Residual Fuel From Bottoms (>600°F) of Last MRCC Run	 1190
Sample(s) Retained*	25.75
 Gasoline Sample From JP-4 Reformate	 32.1

*Approximately 10 pounds additional sample removed during
characterization of residual fuel oil.

TABLE 67

**INVENTORY OF MATERIAL REMAINING
PENDING DISPOSITION INSTRUCTIONS
(All Weights In Pounds)**

Fractionation Overhead (<600°F)	2126.0
Washed Extraction Raffinate	4887.0
CHST Recycle Product	738.0
Bottoms Remaining From Fractionation of Off-Specification JP-8 GCHT Product	130

3. DISCUSSION

The net gas weight recoveries shown in the units involving hydrogen processing are subject to the previously discussed variations in inlet gas composition, and the resulting uncertainties must be taken into account when assessing the significance of these values. Variation in the weights obtained between individual scales also arise, but are of relatively low order.

The relatively large lineout charge shown in Table 59 for the crude shale hydrotreating operation arose from initial start-up problems, and from subsequent lineouts after catalyst changes. Fractionation losses, as noted, arose from drum handling and from losses of non-condensable material during the reduced pressure fractionation.

As indicated in Table 60, the major loss in the modified reduced crude conversion (MRCC) unit occurred during lineout and shutdown when changing from one feedstock to another. Filtration losses, incurred when the MRCC unit product was filtered to remove catalyst fines prior to fractionation, are also present in addition to the fractionation losses previously discussed. The reader will note that data from the cycle oil hydrotreating operation (COHT) is included in the data for the MRCC unit by virtue of the origin of the feed to the COHT and the disposition of product from this unit.

The extract yield cited in Table 61 was calculated from the results of neutralization of an aliquot portion of extractor run 2.

Starting with the guardcase hydrotreater, the accounting data reflect the parallel processing of the feedstocks used to produce the JP-8 and JP-4 sample pools. The data shown in Table 62 reflect the handling losses and fractionation losses incurred. The high gas loss incurred in processing the JP-4 pool resulted from the high percentage (~60%) of recycle processing used to produce an unacceptable product.

The major loss shown for the reforming of the JP-8 pool in Table 63 occurred through leaks in the reactor which developed due to the increasingly high temperatures of operation required as the run progressed, and by failure to recover all possible condensate from the off-gas stream. These deficiencies were corrected prior to reforming of the JP-4 pool.

As shown in Table 64, the absence of a unit shutdown between aromatic saturation of the JP-8 and JP-4 sample resulted in some liquid imbalance in favor of the JP-8 pool. The "transition bottoms" cited in the JP-8 pool consisted of intermediate stabilized product obtained when changing feeds from the JP-8 to JP-8 Broadrange. This material was, subsequently, blended off into the final turbine fuels.

Blending of the components of the final turbine fuels is shown in Table 65. The weights of other fuel samples submitted are detailed in Table 66. Some scale-to-scale blending variations are apparent in comparing these values with those listed previously in the process units.

The product weights shown in Table 67 represent the results of a physical inventory carried out at Ashland Petroleum R&D Pilot Plant. These materials are presently being stored pending disposition instructions from the Air Force.

